This quarterly report presents current information on the timber situation in Alaska, Washington, Oregon, California, Montana, Idaho, and British Columbia, including data on lumber and plywood production and prices; timber harvest; employment in forest products industries; international trade in logs, pulpwood, chips, lumber, and plywood; log prices in the Pacific Northwest; volume and average prices of stumpage sold by public agencies; and other related items.

Historical data for the years before 1969 are in the 1979 issues of "Production, Prices, Employment, and Trade in Northwest Forest Industries."

Cooperation in supplying data has been received from a number of sources. These include the U.S. Department of Agriculture, Forest Service, Forest Resources Economics Research Staff in Washington, D.C.; Washington State Department of Natural Resources and Employment Security Department; Oregon State Department of Forestry and Department of Employment; California State Department of Employment and Department of Conservation; Montana State Forester and State Employment Service; Idaho State Department of Public Lands and Department of Employment; Alaska State Department of Labor and Department of Natural Resources of the Division of Lands; U.S. Department of Commerce; U.S. Department of the Interior, Bureau of Land Management and Bureau of Indian Affairs; British Columbia Department of Industrial Development, Trade, and Commerce; and a number of private industry associations, firms, and individuals.

The statistical data are from secondary sources and are brought together to make such information more readily available. Sources are indicated for each table and can be contacted directly for means used in data collection.

KEYWORDS: Forestry business economics, lumber, plywood, timber volume, stumpage sales, employment, marketing, log exports.

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TABLES INCLUDED IN THIS SERIES OF REPORTS, FREQUENCY OF PUBLICATION, AND MOST RECENT QUARTER PUBLISHED

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Washington and Oregon timber harvest, by ownership, 1969-78	А	Second quarter 1980

 ^{1/}A: Published annually as data become available.
 B: Published biannually as data become available.
 P: Published periodically as data become available.

Q: Published quarterly as data become available.

Montana and Idaho timber harvest by ownership, 1969-79	А	Third quarter 1980
British Columbia timber harvest, 1969-79	А	Third quarter 1980
Alaska timber harvest on public lands, by ownership, 1969-79	Α	Third quarter 1980
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Noble fir log prices, western Washington and northwestern Oregon, 1969-79	А	Second quarter 1980
White fir log prices, western Washington and northwestern Oregon, 1969-79	А	Second quarter 1980
Sitka spruce log prices, western Washington and northwestern Oregon, 1969-79	А	Second quarter 1980
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YEAR	TOTAL SOFTWOOD LUMBER	WESTERN WASHINGTON AND WESTERN OREGON	CALIFORNIA REDWOOD REGION	INLAND REGION1	U.S. SOFTWOOD PLYWOOD PRODUCTION ²
		Million board	feet		Million sq ft, 3/8-inch basis
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980	19,076 20,631 21,830 22,267 19,425 17,778 20,611 21,558 20,780 20,045 16,429	7,475 8,283 8,983 9,074 7,777 7,139 8,322 8,796 8,845 8,427 7,165	2,374 2,329 2,452 2,629 2,675 2,194 2,500 2,453 1,902 1,838 1,631	9,227 10,019 10,395 10,564 8,973 8,445 9,789 10,309 10,033 9,780 7,633	14,277 16,635 18,324 18,305 15,878 16,050 18,440 19,677 19,936 20,022 16,573
January February March	1,402 1,353 1,520	614 590 655	129 132 125	659 631 740	1,501 1,491 1,618
Total, 1st quarter	4,275	1,859	386	2,030	4,610
April May June					
Total, 2d quarter					
July August September					
Total, 3d quarter					
October November December					
Total, 4th quarter					
1981 total					
From 4th quarter 1980	4.6	1st quarter 196	31 change, in p -4.0	ercent · · 3.2	3.5
1st quarter 1980	-3.9	-9.0	-10.0	2.8	4.8

Source--Western Wood Products Association, Portland, Oregon (western Washington and western Oregon, inland region), National Forest Products Association, Washington, D.C. (California redwood region), and American Plywood Association, Tacoma, Washington (U.S. softwood plywood data).

 $^{^1}$ Inland region includes eastern Washington, eastern Oregon, California (except redwood region), Nevada, Idaho, Montana, Wyoming, Utah, Colorado, Arizona, New Mexico, and a portion of South Dakota.

²Data for 1974 and 1975 are based in part on sampling.

YEAR	TOTAL	OREGON	WASHINGTON	CALIFORNIA	COLORADO	STATES ¹	STATES ²
1970	14,291.OR	7,439.1	1,804.9	826.8	891.2	3,315.0	14.0
1971	16,642.1R	8,147.9	2,070.0	984.3	1,022.8	4,410.1	7.0
1972 1973	18,323.7 18,304.6	8,634.9 8,518.6	2,251.1 2,232.5	1,050.7 963.8	1,068.2 1,031.0	5,318.8 5,558.7	0
1974	15,878.3	7,055.6	1,853.3	843.6	995.7	5,130.1	0
1975	16,050.3	6,927.4	1,723.7	649.6	1,074.1	5,675.5	0
1976 1977	18,440.0	7,917.0	1,894.0	603.0	1,212.0	6,814.0	0
1977	19,376.2 19,964.4	8,109.2 8,226.4	` 2,013.0 2,084.2	552.0 510.7	1,255.0 1,245.0	7,447.0 7,898.1	0 0
19 79 1980	19,653.0 16,468.0	7,929.0 6,179.0	1,727.0 1,333.0	463.0 319.0	1,205.0 1,088.0	8,329.0 7,393.0	0 156.0
1300	10,400.0	0,1/3.0	1,333.0	319.0	1,000.0	7,393.0	130.0

Source--American Plywood Association.

 $^{^{1}}$ Southern States include Alabama, Arkansas, Florida, Georgia, Louisiana, Maryland, North Carolina, Oklahoma, South Carolina, Texas, and Virginia.

² Northern States include Maine, Michigan, Minnesota, Wisconsin.

R = revised.

YEAR	DIMENSION, 25 PCT. STD. AND BTR., 2 BY 4 RL, GREEN, S4S, F.O.B. Mill	PONDEROSA PINE BOARDS, NO. 3, 1 BY 12 RL, DRY, S4S, F.O.B. MILL	PONDEROSA PINE NO. 2 SHOP, 6/4 RWRL, S2S, DRY, F.O.B. MILL	DIMENSION STD. AND BTR., 2-IN RWRL, DRY, S4S, F.O.B. MILL	DIMENSION STD. AND BTR., 2-IN RWRL, DRY, S4S, F.O.B. MILL
1970 1971	74.13	84.62	119.82	89.34	77.77
1972	97.77 117.48	96.44 130.94	152.26 179.94	112.38 141.20	101.96 128.93
1973	152.23	179.29	225.65	175.47	167.87
1974	135.05	167.47	244.94	155.28	147.05
1975 1976	137.64 167.98	143.28	196.89	149.29	137.55
1977	204.76	184.31 231.53	314.44 377.24	184.37 224.34	175.56 206.70
1978	227.22	$\frac{1}{258.44}$	460.00	248.32	237.30
1979	251.34	317.26	478.27	283.06	268.10
1980	197.72	287.52	460.02	223.08	211.23
1981 January	NA	NA	NA	NA	NA
February	NA NA	NA NA	NA NA	NA NA	NA NA
March	NA	NA	NA	NA	NA
Average, 1st quarter	NA	NA	NA	NA	NA NA
April					
May			•		
June					·
Average, 2d quarter					
July August September					
Average, 3d quarter					
October November December					
Average, 4th quarter					
1981 average					
		1st qua	rter 1981 change, in perce	nt_	
From					
4th quarter 1980 1st quarter 1980	NA NA	NA NA	NA NA	NA NA	NA NA

Source-U.S. Bureau of Labor Statistics.

NA = not available.

 $¹_{11-month}$ average.

YEAR	INTERIOR, 1/4-INCH, AD, F.O.B. MILL	EXTERIOR, 3/8-INCH, AC, F.O.B. MILL	INTERIOR SHEATHING, 1/2-INCH, STD. EXT. GLUE, F.O.B. MILL ¹
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 January February March	64.34 72.58 87.79 111.61 125.79 131.84 144.97 162.48 191.92 201.66 190.36 NA NA	93.36 103.79 126.44 174.50 158.27 173.00 206.61 226.44 258.51 272.90 253.36 NA NA	118.30 138.23 128.72 135.07 155.86 195.37 214.38 2/205.79 193.51 NA NA
Average, 1st quarter April May	NA	NA ,	NA
June Average, 2d quarter July August September			
Average, 3d quarter October November December			
Average, 4th quarter 1981 average			
From 4th quarter 1980 1st quarter 1980	1st NA NA	quarter 1981 change, i NA NA	in percent NA NA

Source--U.S. Bureau of Labor Statistics.

NA = not available.

¹Established January 1972.

²¹¹-month average.

16700	101110			TOTAL		11000013	TOTAL	/ NODOC13	1 KODOC 13	TOTAL	1 KODOC 13	1 10000013
1970 1971 1972 1973 1974 1975 1976 1977	138.2 141.2 150.2 155.3 152.1 137.2 150.9 159.2	109.0 113.8 122.5 127.9 124.5 110.8 123.4 131.4	29.2 27.4 27.7 27.4 27.6 26.4 27.5	62.0 61.5 65.5 66.8 67.3 60.4 68.4 71.6	42.2 43.4 47.3 49.1 49.7 43.8 51.0 53.9	19.8 18.1 18.2 17.7 17.6 16.6 17.4 17.7	76.2 79.7 84.7 88.5 84.8 76.8 82.5	66.8 70.4 75.2 78.8 74.8 67.0 72.4	9.4 9.3 9.5 9.7 10.0 9.8 10.1	 3.4 3.6	2.8 2.8 2.8 2.3 2.5 2.0 2.3 2.2	1/ 1/ 1/ 2/ 2/ 2/ 1.1 1.4
1978 1979 1980	159.3 159.0 141.2	136.5 133.4 113.4	22.8 25.6 27.8	69.1 68.4 62.5	55.1 52.6 45.0	14.0 15.8 17.5	90.2 90.6 78.7	81.4 80.8 68.4	8.8 9.8 10.3	2.9 3.0 3.4	1.8 2.0 2.4	1.1 1.0 1.0
1981 January February March	136.9 136.6 135.4	109.4 109.3 108.4	27.5 27.3 27.0	61.7 61.9 61.2	44.4 44.7 44.4	17.3 17.2 16.8	75.2 74.7 74.2	65.0 64.6 64.0	10.2 10.1 10.2	2.1 2.3 2.8	1.2 1.4 1.9	.9 .9 .9
Average, 1st quarter	136.3	109.0	27.3	61.6	44.5	17.1	74.7	64.5	10.2	2.4	1.5	.9
April May June												
Average, — 2d quarter	,		ş								<u></u>	
July August September												
Average, 3d quarter								***************************************				
October November December												
Average, 4th quarter												18.87
1981 average												
From					1st quar	ter 1981 chai	nge in empl	oyment				
4th quarter 1980 1st quarter	-3.2R	-2.1	-1.1R	8R	.2R	-1.OR	-2.4	-2.3	1	4	4	0
1980	-14.6R	-13.7	9R	-4.6R	-3.9R	7R	10.OR	-9.8R	2	.5	.1	. 4

Source—State employment agencies. Includes both covered and noncovered employment. The lumber and wood products industry includes logging, lumber, plywood, poles and piling, and miscellaneous wood products (excludes furniture). The paper and allied products industry includes pulp, paper, paperboard, and building board products. Since April 1974, employment data have been based on place of residence.

 $^{1}\mathrm{Before}$ 1973, data for the pulp and allied products industry are included in the lumber and wood products industry.

 2 Withheld to avoid disclosure.

R = revised.

YEAR	TOTAL	LUMBER AND WOOD PRODUCTS	PAPER AND ALLIED PRODUCTS
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	84.8 86.0 90.3 90.2 88.2 87.3 96.6 104.2 107.1	48.1 50.5 52.4 54.1 50.9 52.8 59.9 66.6 69.9 68.7	36.7 35.5 37.9 36.1 37.3 34.5 36.7 37.6 37.2
January February March	101.9 101.8 102.1	62.5 62.4 62.4	39.4 39.4 39.7
Average, Ist quarter	101.9	62.4	39.5
April May June	100.5 98.7 100.4	61.1 59.8 61.9	39.4 38.9 38.5
Average, 2d quarter	99.8	60.9	38.9
July August September	102.0 102.1 103.1	63.6 63.8 64.6	38.4 38.3 38.5
Average, 3d quarter	102.4	64.0	38.4
October November December	102.7 101.2 98.8	64.6 63.3 60.9	38.1 37.9 37.9
Average, 4th quarter	100.9	62.9	38.0
1980 average	101.3	62.6	38.7
	4th	n quarter 1980 change	in employment
From 3d quarter 1980 4th quarter 1979	-1.5 -6.4	-1.1 -5.1	4 -1.3
		Year 1980 change in er	mployment— — —
From year 1979	-6.5	-6.1	4

Source--State of California, Department of Employment. Since April 1974, data have been based on place of residence.

YEAR	LUMBER AND WOOD PRODUCTS	PAPER AND ALLIED PRODUCTS	TOTAL	LUMBER AND WOOD PRODUCTS	PAPER AND ALLIED PRODUCTS
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980	8.2 8.7 9.2 9.8 9.5 8.1 9.1 9.3 10.7 11.0 8.8	1/ T/ I/ I/ T/ I/ T/ T/ T/	13.8 14.8 15.2 16.3 15.7 16.8 18.6 19.0 20.1 19.9	12.8 13.7 14.1 15.1 14.6 15.7 17.4 17.8 18.8 18.5	1.0 1.1 1.1 1.2 1.1 1.1 1.2 1.2 1.3 1.4
January February March	9.1 8.9 8.8	1/ 1/ 1/	17.2 17.2 16.1	15.7 15.7 14.6	1.5 1.5 1.5
Average, 1st quarter	8.9	1/	16.8	15.3	1.5
April May June					
Average, 2d quarter		**************************************			
July August September					
Average, 3d quarter				e communicación de la comm	
October November December					
Average, 4th quarter			·		
1981 average		1st quarte	r 1981 change	e in employment – –	
From 4th quarter 1980 1st quarter 1980	.4 8R		-1.3 6R	-1.3 7R	0. .1R

Source--State employment agencies. Since April 1974, employment data have been based on place of residence.

 ${}^1\!\text{Withheld}$ to avoid disclosing figures for individual companies.

R = revised.

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	PORT ORF ORD- CE DAR	OTHER SOFTWOODS
					TO ALL	COUNTRIES					
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980	2,216,110 1,837,173 2,637,148 2,639,210 2,189,367 2,225,487 2,737,074 2,555,615 2,847,394 3,233,652	452,655 416,453 767,496 864,474 715,514 765,840 945,649 966,763 1,139,267 1,309,179	41,260 34,390 36,907 20,956 17,481 24,361 26,576 16,721 24,493 22,693	1,722,195 1,386,330 1,832,745 1,753,770 1,456,372 1,435,286 1,764,849 1,572,131 1,683,634 1,901,780	1,579,185 1,319,809 1,907,235 1,833,293 1,423,570 1,427,387 1,792,944 1,674,860 1,915,979 2,249,963	308,466 294,430 566,487 555,324 404,884 437,290 527,889 556,419 619,500 732,392	1,270,719 1,025,379 1,340,748 1,277,969 1,018,686 990,097 1,265,055 1,118,441 1,296,479 1,517,571	636,925 517,364 729,913 805,917 765,797 798,100 944,130 880,755 931,415 983,689	144,189 122,023 201,009 309,150 310,630 328,550 417,760 410,344 519,767 576,787	41,260 34,390 36,907 20,966 17,481 24,361 26,576 16,721 24,493 22,693	451,476 360,951 491,997 475,801 437,686 445,189 499,794 453,690 387,155 384,209
1st qtr. 2d qtr. 3d qtr. 4th qtr.	827,738 793,840 508,640 501,599	369,910 358,563 265,986 267,751	3,440 4,704 2,249 1,907	454,388 430,573 240,405 231,941	547,829 539,841 309,541 301,927	193,213 189,551 132,270 130,039	354,616 350,290 177,271 171,888	279,909 253,999 199,099 199,672	176,697 169,012 133,716 137,712	3,440 4,704 2,249 1,907	99,772 80,283 63,134 60,053
1980 total	2,631,817	1,262,210	12,300	1,357,307	1,699,138	645,073	1,054,065	932,679	617,137	12,300	303,242
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	519,222	251,035	5,505	262,682	333,359	128,237	205,122	185,863	122,798	5,505	57,560
1981 total											
					JAP	AN					
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	2,144,332 1,710,299 2,391,163 2,455,485 1,975,575 2,014,244 2,547,037 2,348,325 2,521,885 2,959,726	430,634 390,978 692,308 822,160 638,225 732,264 901,911 933,813 1,103,562 1,279,177	41,254 34,390 36,907 20,966 17,342 24,361 24,573 16,721 22,814 20,611	1,672,444 1,284,931 1,661,948 1,612,359 1,320,008 1,257,619 1,620,553 1,397,791 1,395,509 1,659,938	1,514,695 1,197,011 1,678,846 1,663,203 1,237,653 1,255,817 1,623,064 1,496,627 1,630,247 1,998,315	290,158 271,763 496,201 520,373 341,890 410,721 491,451 526,255 509,654 705,921	1,224,537 925,248 1,182,645 1,142,830 895,763 845,096 1,131,613 970,372 1,040,593 1,292,394	629,637 513,288 712,317 792,282 737,922 758,427 923,973 851,698 891,638 961,411	140,476 119,215 196,107 301,787 296,335 321,543 410,460 407,558 513,908 573,256	41,254 34,390 36,907 20,966 17,342 24,361 24,573 16,721 22,814 20,611	447,907 359,683 479,303 469,529 424,245 412,523 488,940 427,419 354,916 367,544
1st qtr. 2d qtr. 3d qtr. 4th qtr.	758,470 727,929 460,916 397,007	363,052 352,551 250,857 208,947	3,440 4,704 2,249 1,907	391,978 370,674 207,810 186,153	491,160 481,535 270,364 245,435	189,294 185,236 120,840 107,235	301,866 296,299 149,524 138,200	267,310 246,394 190,552 151,572	173,758 167,315 130,017 101,712	3,440 4,704 2,249 1,907	90,112 74,375 58,286 47,953
- 1980 total	2,344,322	1,175,407	12,300	1,156,615	1,488,494	602,605	885,889	855,828	572,802	12,300	270,726
1981— 1st qtr. 2d qtr. 3d qtr. 4th qtr.	423,412	221,734	5,505	196,173	252,904	107,354	145,550	170,508	114,380	5,505	50,623

1981 total

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS FIR	PORT - ORFORD- CEDAR	OTHER SOFTWOODS
					TO CA	NADA					
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	27,997 55,712 170,582 72,164 73,664 58,506 48,289 15,698 12,638 24,124	11,171 12,332 43,294 22,265 39,060 16,793 14,803 9,531 9,361 7,737	 	16,826 43,380 127,288 49,899 34,604 41,713 33,486 6,167 3,277 16,387	27,997 55,712 159,359 72,164 73,664 58,506 48,289 15,698 12,638 24,124	11,171 12,332 43,294 22,265 39,060 16,793 14,803 9,531 9,361 7,737	16,826 43,380 116,065 49,899 34,604 41,713 33,486 6,167 3,277 16,387	11,223			11,223
1st qtr. 2d qtr. 3d qtr. 4th qtr.	153 247 264 321	77 49 61 208		76 98 203 113	153 247 264 321	77 49 61 208	76 198 203 113	 	 		
1980 total	985	395		590	985	395	590				
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	634	239		395	634	239	395				
1981 total											
					TO SOUTH	KOREA					
1970 1971 1972 1973 1974 1975 1976 1977 1978	32,336 63,757 47,554 101,929 137,665 79,022 130,069 187,967 307,865 245,314	5,140 6,331 4,419 15,175 36,308 13,946 26,454 21,201 24,844 20,342	 	27,196 57,426 43,135 86,754 101,357 65,076 103,615 166,766 283,021 224,972	26,839 62,757 46,304 96,680 111,580 42,100 117,007 162,252 271,887 227,072	3,138 6,331 4,419 12,063 23,378 9,100 21,068 20,418 20,426 18,653	23,701 56,426 41,885 84,617 88,202 33,000 95,939 141,834 251,461 208,419	5,497 1,000 1,250 5,249 26,085 36,922 13,062 25,715 35,978 18,242	2,002 3,112 12,930 4,846 5,386 783 4,418 1,689		3,495 1,000 1,250 2,137 13,155 32,076 7,676 24,932 31,560 16,553
980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	67,479 59,802 32,084 32,022	5,386 1,094 1,861 3,455		62,093 58,708 30,223 28,567	56,375 53,477 27,547 26,589	3,782 677 1,861 3,229	52,593 52,800 25,686 23,360	11,104 6,325 4,537 5,433	1,604 417 226		9,500 5,908 4,537 5,207
1980 total	191,387	11,796		179,591	163,988	9,549	154,439	27,399	2,247	_	25,152
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	47,994	3,781	<u>.</u>	44,213	47,097	3,279	43,818	897	502		395
1981 total				<u></u>							
					TO MAINLA	ND CHINA					
1980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	3,584 14,357 69,844	3,584 13,101 53,216	=======================================	1,256 16,628	3,584 10,733 28,954	3,584 9,508 18,792	1,225 10,162	3,624 40,890	 3,593 34,424		31 6,466
1980 total	87,785	69,901		17,884	43,271	31,884	11,387	44,514	38,017		6,497
981— 1st qtr. 2d qtr. 3d qtr. 4th qtr	43,381	23,684	-	19,697	31,378	16,159	15,219	12,003	7,525	***	4,478
 1981 total											

Source--U.S. Department of Commerce. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOF TWOODS
					TO ALL	COUNTRIES					
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	280,920 233,304 358,713 694,602 612,521 603,854 775,113 826,698 992,207 1,408,036	54,109 49,773 101,467 209,417 194,137 202,377 266,523 311,269 413,645 624,090	13,611 10,926 12,089 15,451 17,556 16,758 20,086 17,049 24,923 24,419	213,200 172,605 245,157 469,734 400,828 384,759 488,504 498,380 553,639 831,527	193,476 162,343 252,839 449,902 364,962 376,705 490,246 526,412 637,818 991,513	37,015 35,141 73,175 120,796 103,586 111,919 141,989 171,541 212,305 331,874	156,461 127,202 179,664 329,106 271,376 264,787 348,257 354,871 425,513 659,639	87,444 70,961 105,874 244,700 237,559 227,148 284,867 300,286 354,389 488,523	17,094 14,632 28,292 88,621 90,551 90,418 124,534 139,728 201,340 292,216	13,611 10,926 12,089 15,451 17,556 16,758 20,087 17,049 24,923 24,419	56,739 45,403 65,493 140,628 129,452 119,972 140,247 143,509 128,126 171,188
1st qtr. 2d qtr. 3d qtr. 4th qtr.	425,175 407,304 246,182 230,197	192,752 186,597 130,256 125,293	5,368 5,857 2,800 2,571	227,055 214,850 113,126 102,333	276,019 273,041 149,637 136,827	97,683 96,761 63,905 59,395	178,336 176,280 85,732 77,432	149,156 134,263 96,545 93,370	95,069 89,836 66,351 65,898	5,368 5,857 2,800 2,571	48,719 38,570 27,394 24,901
1980 total	1,308,858	634,898	16,596	657,364	835,524	317,744	517,780	473,334	317,154	16,596	139,584
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	233,027	118,446	8,158	106,423	144,701	60,167	84,534	88,326	58,279	8,158	21,889
1981 total						· · · · · · · · · · · · · · · · · · ·					
					TO	JAPAN					
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980—	273, 988 219,543 335,703 664,363 569,494 560,754 734,412 776,630 908,627 1,387,602	52,051 46,966 94,210 201,944 177,961 195,469 256,673 303,248 404,134 612,160	13,608 10,926 12,089 15,451 17,500 16,758 17,918 17,049 22,763 22,271	208,329 161,651 229,404 446,968 374,033 348,527 459,821 456,333 481,730 753,171	187,237 149,120 231,593 422,715 338,296 341,885 457,248 484,006 566,494 910,338	35,294 32,756 66,800 115,022 90,400 107,149 134,894 164,626 204,832 323,034	151,943 116,364 164,793 307,693 247,896 234,736 322,354 319,380 361,662 587,304	86,751 70,423 104,110 241,648 231,198 218,869 277,164 292,624 342,133 477,264	16,757 14,210 27,410 86,922 87,561 88,320 121,779 138,622 199,302 289,126	13,608 10,926 12,089 15,451 17,500 16,758 17,918 17,049 22,763 22,271	56,386 45,287 64,611 139,275 126,137 113,791 137,467 136,953 120,068 165,867
lst qtr. 2d qtr. 3d qtr. 4th qtr.	398,458 379,364 225,699 187,354	189,888 182,562 122,119 98,915	5,368 5,857 2,800 2,571	203,202 190,945 100,780 85,868	254,399 248,492 132,636 114,842	96,324 94,003 57,754 49,278	158,075 154,489 74,882 65,564	144,059 130,872 93,063 72,512	93,564 88,559 64,365 49,637	5,368 5,857 2,800 2,571	45,127 36,456 25,898 20,304
1980 total	1,190,875	593,484	16,596	580,795	750,369	297,359	453,010	440,506	296,125	16,596	127,785
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	197,679	106,012	8,158	83,509	115,580	51,466	64,114	82,099	54,546	8,158	19,395

1981 total

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD~ CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOF TWOODS	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
					TO CA	NADA		The sale of the sa	·	· · · · · · · · · · · · · · · · · · ·	
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	2,023 4,892 14,041 9,593 13,821 8,313 7,908 3,545 2,933 7,223	863 1,240 2,984 2,900 8,239 2,937 2,733 2,154 2,129 2,435		1,160 3,652 11,057 6,693 5,582 5,376 5,175 1,391 804 4,788	2,023 4,892 13,349 9,593 13,821 8,313 7,908 3,545 2,933 7,223	863 1,240 2,984 2,900 8,239 2,937 2,733 2,154 2,129 2,435	1,160 3,652 10,365 6,693 5,582 5,376 5,175 1,391 804 4,788	692	 		692
1st qtr. 2d qtr. 3d qtr. 4th qtr.	44 77 88 114	22 23 20 68		22 54 68 46	44 77 88 114	22 23 20 68	22 54 68 46	 			
1980 total	323	133		190	323	133	190				
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	253	107		146	253	107	146			~~	~
1981 tota)											
					TO SOUTH	KOREA					
1970 1971 1972 1973 1974 1975 1976 1977 1978	3,659 7,950 5,094 18,506 28,225 14,757 27,546 44,949 76,839 80,173	559 728 469 3,468 7,303 2,688 5,664 4,811 6,392 6,982	 	3,100 7,222 4,625 15,038 20,922 12,069 21,882 40,138 70,447 73,191	3,174 7,863 4,939 17,290 22,552 7,912 24,400 38,738 67,974 73,751	416 728 469 2,725 4,714 1,648 4,350 4,672 5,333 6,378	2,758 7,135 4,470 14,565 17,838 6,264 20,050 34,066 62,641 67,373	485 87 155 1,216 5,673 6,845 3,146 6,211 8,865 6,422	143 743 2,589 1,040 1,315 139 1,059 604	 	342 87 155 473 3,084 5,805 1,831 6,072 7,806 5,818
1980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	25,471 23,687 11,590 10,927	1,903 330 617 1,266	 	23,568 23,357 10,973 9,661	21,448 21,421 10,237 9,002	1,306 178 617 1,178	20,142 21,243 9,620 7,824	4,023 2,266 1,353 1,925	597 152 88	 	3,426 2,114 1,353 1,837
1980 total	71,675	4,116		67,559	62,108	3,279	58,829	9,567	837	**-	8,730
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	16,024	1,276		14,748	15,720	1,108	14,612	304	168		136
1981 total											
					TO MAINLA	ND CHINA					
1980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	2,553 8,153 30,727	2,553 7,456 24,276	 	 697 6,451	2,553 6,202 12,571	2,553 5,514 8,625	 688 3,946	1,951 18,156	1,942 15,651		9 2,505
1980 total	41,433	34,285		7,148	21,326	16,692	4,634	20,107	17,593		2,514
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	17,796	1,040	~~	7,392	12,594	6,991	5,603	5,202	3,413		1,789

Source—U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

UARTER 1970 1971 1972 1973 1974 1975	126.76 126.99 136.02 263.19 279.77 271.34 283.19 323.48	DOUGLAS- FIR 119.54 119.52 132.21 242.25 271.33	PORT ORFORD- CEDAR 329.88 317.70 327.56	OTHER SOFTWOODS	ALL SPECIES TO ALL COL	DOUGLAS- FIR JNTRIES	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOOD
1971 1972 1973 1974 1975 1976	126.99 136.02 263.19 279.77 271.34 283.19	119.52 132.21 242.25	317.70	123.80	TO ALL COL	INTRIES					
1971 1972 1973 1974 1975 1976	126.99 136.02 263.19 279.77 271.34 283.19	119.52 132.21 242.25	317.70	123.80							
1972 1973 1974 1975 1976	136.02 263.19 279.77 271.34 283.19	132.21 242.25	317.70		122.52	120.00	123.13	137.29	118.55	329.88	125.67
L973 L974 L975 L976	263.19 279.77 271.34 283.19	242.25	227 56	124.51 133.76	123.00	119.35	124.05	137.16	119.91	317.70	125.79
.974 .975 .976	279.77 271.34 283.19		327.30	133.76	132.57	129.17	134.00 257.52	145.05	140.75	327.56	133.12
.975 .976	271.34 283.19		736.97 1,004.29	267.84 275.22	245.41 263.40	217.52 255.84 255.94	266.40	303.63 310.21	286.66 291.51	736.97 1,004.29	133.12 295.56 295.76
976	283.19	264.20	687 90	268.07	263.40	255.94	267.43	284.61	275.20	687.90	269.49
	222.40	281.84	687.90 755.83	276.80	263.91 273.43	268.98	275.29	301.73	298.10	755.83	280.61
977		321.97	1.019.62	317.01	314.30	308.29	317.26	340.94	340.51	1,019.62	316.32
978	348.46	363.08	1,017.56	328.84	332.89	342.70	328.21	380.48	387.37	1,017.56	330.94
979	435.43	476.70	1,076.06	437.24	440.68	453.14	434.67	496.62	506.62	1,076.06	445.56
.980	C12 CC	E21 00	1 500 44	400 60	F03 04	505 57	502.90	532.87	630 04	1 550 44	488.30
1st qtr. 2d qtr.	513.66 513.08	521.08 520.40	1,560.44 1,245.03	499.69 498.99	503.84 505.78	505.57 510.48	503.24	528.60	538.04 531.54	1,560.44 1,245.03	488.30
3d qtr.	484.00	489.71	1,245.05	470.56	483.41	483.14	483.62	484.91	496.21	1,245.05	433.90
4th gtr.	458.93	467.95	1,348.42	441.20	453.18	456.75	450.48	467.62	478.52	1,348.42	414.65
· -			·	· · · · · · · · · · · · · · · · · · ·							
1980 average	497.32	503.00	1,349.27	484.32	491.73	492.57	491.22	507.50	513.91	1,349.27	460.31
981						·					
lst atr.	448.80	471.83	1,481.97	405.14	434.07	469.18	412.11	475.22	474.59	1,481.97	380.28
2d qtr.											
3d qtr. 4th qtr.											
4cm qur.											
1981 average											
					TO JAP	AN	-				
1970	127.77	120.87	220.06	124.57	123.61	121.64	124.08	137.78	119.29	329.86	126.00
1971	128.36	120.12	317.70	125.81	124.58	120.53	125.77	137.20	119.19	317.70	125.89 125.91
972	140.39	136.08	329.86 317.70 327.56	138 03	137.95	134.62	139.34	146.16	139 77	327.56	134.80 296.63 297.32
973	270.56	245.63	736.97 1,009.12	277.21	254.16 273.34	221.04	269.24	305.00	288.03	736.97 1,009.12	296.63
974	288.27	278.84	1,009.12	283.36	273.34	264.41	276.74	313.31	295.48	1,009.12	297.32
975	278.39	266.94	687.90	277.13	272.24	260.88	277.76	288.58	274.68	687.90 729.17	275.84
976	288.34	284.59	729.17 1,019.62	283.74	281.72	274.48	284.86	299.97	296.69	729.17	281.15
.977 .978	330.72 360.30	324.74 366.21	997.76	326.47 345.20	323.40 347.49	312.83 347.38	329.13 347.55	343.58 383.71	340.13 387.82	1,019.62 997.76	320.42 338.30
979	468.83	478.56	1,080.54	453.73	455.55	457.61	454.43	496.42	504.36	1,080.54	451.28
980	400.00	-170.30	1,000.54	433.73	433.33	457.01	454.45	430.42	301.30	1,000.04	731.20
lst gtr.	525.34	523.03	1.560.44	518.40	517.96	508.86	523.66	538.92	538.47 529.30	1,560.44	500.79 490.17
2d qtr.	521.16	523.03 517.83	1,560.44 1,245.03	515.13R	516.04R	507.48	523.66 521.39	531.15	529.30	1,245.03	490.17
3d atr.	489.67	486.80	1,245.05	484.96	490.58	477.93	500.80	488.39	495.05	1,245.05	444.33
4th qtr.	471.92	473.40	1,348.42	461.28	467.91	459.53	474.42	478.40	488.02	1,348.42	423.41
1980 average	507.98	504.92	1,349.27	502.15	504.11	493.35	511.36	514.71	516.98	1,349.27	472.01
981											
1st qtr. 2d qtr. 3d qtr. 4th qtr.	466.87	478.10	1,481.97	425.69	457.01	479.40	440.49	481.50	476.89	1,481.97	383.13

1981 average

YEAR AND QUARTER	ALL SPECIES	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- FIR	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- F IR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
	***				TO CAN	ADA					
1970 1971 1972 1973 1974 1975 1976 1977 1978	72.26 87.80 82.31 132.94 187.62 142.09 163.76 225.82 232.08 299.41	77.23 100.55 68.93 130.26 210.93 174.89 184.62 226.00 227.43 314.72		68.96 84.18 86.86 134.14 161.31 128.88 154.54 225.56 245.35 292.78	72.26 87.80 83.77 132.94 187.62 142.09 163.76 225.82 232.08 299.41	77.23 100.55 68.93 130.26 210.93 174.89 184.62 226.00 227.43 314.72	68.96 84.18 80.30 134.14 161.31 128.88 154.54 225.56 245.35 292.18	61.66 			61.66
1980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	289,39 313,79 334,95 356,11	290.00 476.61 333.44 329.61	 	288.78 273.49 335.40 404.89	289.39 319.79 334.95 356.11	290.00 476.61 333.44 329.61	288.78 273.49 335.40 404.89	 	 		
1980 average	327.92	336.71		322,03	327.92	336.71	322.03				
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	398.65	446.78		369.52	398.65	446.78	369.52				
1981 average		······································									,
					TO SOUTH	KOREA					
1970 1971 1972 1973 1974 1975 1976 1977 1978	113.14 124.70 107.12 181.54 205.03 186.74 211.78 239.13 249.59 326.82	108.63 115.00 106.10 228.47 201.12 192.74 214.11 226.92 257.28 343.23		113.99 125.77 107.22 173.34 206.43 185.46 211.19 240.68 249.02 325.33	118.27 125.30 106.66 178.83 202.12 187.93 208.53 238.75 250.01 324.79	132.53 115.00 106.10 225.89 201.62 181.10 206.47 228.82 261.09 341.93	116.38 126.46 106.72 172.12 202.26 189.82 208.93 240.18 249.11 323.26	88.08 87.00 124.00 231.52 217.47 185.39 240.77 241.53 246.40 352.05	71.18 238.47 200.23 214.61 244.77 177.52 239.70 357.61		97.77 87.00 124.00 221.40 234.41 180.98 238.54 243.54 247.34 351.48
1980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	377.47 396.10 361.23 341.23	353.28 302.01 331.55 366.48	 	379.57 397.86 363.06 338.18	380.46 400.57 371.61 338.57	345.26 263.22 331.55 364.77	382.99 402.33 374.51 334.94	362.32 358.31 298.22 354.27	372.19 365.00 390.86		360.66 357.84 298.22 352.69
1980 average	374.50	348.93		376.18	378.74	343,39	380.92	349.17	372.50		347.09
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	333.88	337.43		333.57	333.78	337,80	333.48	339.09	334.98		344.30
- 1981 average											
					TO MAINLAN	D CHINA					
1980 1st qtr. 2d qtr. 3d qtr. 4th qtr.	712.46 567.93 439.95	712.46 569.15 456.18	 	555.29 388.00	712.46 577.87 434.19	712.46 579.94 458.97	 561.79 388.35	538.53 444.02	540.60 454.65		298.45 387.44
- 1980 average	471.98	490.48		399.69	492.85	523.52	406.96	451.70	462.77		386.95
1981 1st qtr. 2d qtr. 3d qtr. 4th qtr.	410.23	439.28		375.30	401.37	432.62	368.19	433.40	453.59		399.46
– 1981 average								 			

Source—U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

YEAR AND QUARTER	TOTAL	DOUGLAS-FIR	PORT-ORFORD- CEDAR	OTHER SOFTWOODS
		TO ALL COUNTRIES		
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980	192,083 102,408 77,459 104,733 77,735 86,943 109,812 70,902 72,650 65,492	32,531 27,032 18,337 34,454 35,146 52,547 73,924 38,302 49,024 37,551	2,894 2,182 3,418 4,065 8,823 2,483 2,508 2,331 2,880 1,611	156,658 73,194 55,704 66,214 33,766 31,913 33,380 30,269 20,746 26,330
1st quarter 2d quarter 3d quarter 4th quarter	6,517 2,506 13,230 9,419	3,174 2,492 1,621	653	3,343 2,506 10,738 7,145
1980 total	31,672	7,287	653	23,732
1981— 1st quarter 2d quarter 3d quarter 4th quarter	10,123	1,026	360	8,737
1981 total				
		TO JAPAN		
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	175,217 93,281 68,830 94,520 69,271 78,813 96,485 57,815 58,760 57,938	29,965 26,712 15,914 29,261 32,485 48,188 69,395 37,765 48,653 37,411	2,894 2,182 3,418 4,065 8,823 2,483 2,853 2,331 1,757 1,611	142,358 64,387 49,498 61,194 27,963 28,142 24,237 17,719 8,350 18,916
1st quarter 2d quarter 3d quarter 4th quarter	6,517 402 13,194 7,067	3,174 2,492 1,389	 653	3,343 402 10,702 5,025
1980 total	27,180	7,055	653	19,472
1981— 1st quarter 2d quarter 3d quarter 4th quarter	10,105	1,020	360	8,725
 1981 total				

Source—U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

 $^{1}\mbox{Northern}$ California consists of the San Francisco Customs District and includes Monterey, California, and all ports north of Monterey.

YEAR AND QUARTER	ABERDEEN	ANACOR1 BELLING		RETT	LONGVIEW	OL YMP I	PORT A ANGELES	S TACOMA	NORTHEASTERN WASHINGTON	OTHER	TOTAL
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	335.6 297.5 525.1 491.5 396.2 366.8 502.1 402.1 512.2 648.7	66.0 104.1 100.9 84.4 49.3 32.2 30.4 42.4 41.50.5	22 26 25 21 22 23 36 27 23 32 32	4.8 1.4 8.9 0.4 7.7 0.0 7.2 7.7 1.8 2.8	153.3 125.7 221.3 328.7 300.2 261.3 397.4 328.2 325.8 366.1	210.6 120.1 144.6 86.9 61.5 48.6 7.5 68.7 87.1	242.9 212.9 285.6 306.0 273.5 284.7 324.5 304.6 387.2 505.0	356.4 323.1 517.4 511.1 383.0 469.2 623.7 607.6 559.7 601.7	 .2 0 0	79.5 41.0 45.8 54.6 48.4 32.9 28.5 12.0 9.9	1,739.1 1,446.2 2,109.8 2,113.7 1,729.7 1,725.7 2,191.4 2,003.0 2,241.0 2,616.1
1980 1st quarter 2d quarter 3d quarter 4th quarter	144.3 159.5 88.7 105.7	9.8 13.3 6.0 8.9	8 8	9.7 1.0 2.7 3.9	131.2 96.4 83.7 75.7	27.5 30.3 15.2 7.2	102.2 105.3 50.3 37.3	163.5 150.0 95.6 88.0	0 0 0 .1	.8 .5 1.0 .8	679.0 636.3 393.2 377.6
1980 total	498.2	38.0) 28	7.3	387.0	80.2	295.1	497.1	.1	3.1	2,086.1
1981 1st quarter 2d quarter 3d quarter 4th quarter	109,6	7.0	5 6	6.1	61.6	14.7	44.5	90.1	.1	.7	395.0
1981 total		*									
		ST/	TE OF OREG	ON1	· · · · · · · · · · · · · · · · · · ·			NORTHERN CA	LIFORNIA	 	
YEAR AND QUARTER	ASTORIA	COOS BAY	PORTLAND	OTHER	TOTAL	EUREKA	REDWOOD CITY	SACRAMENTO	STOCKTON	OTHER	TOTAL
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter	219.1 194.1 262.6 147.1 159.0 245.7 273.3 210.2 168.4 150.1 49.9 28.9 26.4	114.1 84.2 121.0 155.5 128.1 134.1 144.6 120.1 145.1 128.2 43.8 36.6 25.3	143.9 112.7 115.5 159.8 139.8 137.5 99.5 207.0 277.0 322.0 55.0 92.1 63.7	9.4 21.3 24.8 44.5 28.0 15.4 15.0 17.2	477.1 391.0 508.5 483.7 451.7 561.8 545.4 552.7 605.5 617.5	93.6 65.9 51.9 79.6 67.5 66.6 83.7 39.2 46.1 43.0	4.6 1.2 0 0 0 0 0 0	73.1 35.3 2.8 16.2 9.8 19.9 26.1 25.5 18.4 6.0	2.9 	17.9 0 .9 .2 .2 1.4 6.3 8.2 16.5	192.1 102.4 75.0 140.7 81.3 87.9 21.2 71.0 72.7 65.6
4th quarter	29.5	29.5	65.0	Ö	124.0	4.9	0	3.9 	Ŏ	.6	9.4
1980 total	134.7	135.2	275.8	0	545.7	14.9	0	3.9	.5	12.3	31.6

1981 total

1st quarter

2d quarter 3d quarter 4th quarter 17.1

30.1

77.0

1981--

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

 1 State totals as presented here for Washington and Oregon do not agree with those found in table 8 because customs districts as used in table 8 do not correspond to State boundaries.

124.2

9.7

10.1

YEAR AND		ANACORTE					PORT		NORTHEASTERN		
QUARTER	ABERDEEN	BELLING	IAM EVERE	TT	LONGVIEW ()LYMP IA	ANGELES	TACOMA	WASHINGTON	OTHER	AVERAGE
1970	123.34	126.47	132.6	4	121.51	119.33	118.50	118.44	**-	120.18	122.46
1971	128.46	124.42	125.7	3	126.51	127.76	120.37	116.15		118.62	123.30
1972	134.28	128.21		7	144.82	146.76	129.52	131.82	146.73	123.50	133.86
1973	264.23	211.35	258.6	9	288.82	284.15	215.32	262.90	0	229.45	257.80
1974	266.16	261.07			292.13	282.38	246.79	274.24		262.10	268.58
1975	256.17	297.84			280.90	273.90	253.46	266.63		279.01	266.30
1976	269.90 311.97	293.96			302.53	302.53	261.25 294.59	277.21 327.76	0	252.97	277.26
1977 1978	311.97	296.28 2 9 5.77			336.01 379.57	331.68 347.93	319.97	340.91		263.80 344.67	317.86 339.68
1978	452.52	376.18			518.19	499.12	424.46	428.19		492.38	451.64
1980	432.52	3/0.10	433.4	7	310.15	199.16	727.40	420.13		492.30	431.04
1st quarter	486.07	436.80	484.3	6	534.24	508.39	487.89	544.33	0	570.37	509.72
2d guarter	504.79	415.50			515.32	528.19	486.42	530.12	ō	562.24	507.23
3d quarter	510.11	464.31			469.80	484.09	467.55	504.75	Ö	589.61	487,26
4th quarter	458.69	354.40	430.62	2	488.23	501.15	394.43	491.70	280.95	435.37	460.20
·											
1980 average	490.53	414.44	473.47	7	506.59	510.63	472.08	523.11	280.95	538.84	495.76
1981 1st quarter 2d quarter 3d quarter 4th quarter	408.10	432.05	417.82	?	469.31	514.43	381.89	490.67	307.74	405.07	439.57
1981 average										-	,
		STATE	of oregon ¹						NORTHERN CALIF	DRNIA	
YEAR AND QUARTER	ASTORIA	COOS BAY	PORTLAND	OTHER	AVERAGE	EUREKA	REDWOOD CITY	SACRAMENT	O STOCKTO	N OTHER	AVERAGE
1070	101 50	100.04	100 71		142.46	111 22	00.00	114 04	00.05	00.00	100.01
1970	121.59 117.61	199.84 212.89	128.71 126.33		142.46 140.64	111.22 107.55	90.00 126.58	114.04 110.37	96.95	92.28	109.81 108.76
1971 1972	127.03	194.93		140.31	147.35	107.33	120.56	189.29	179.64	0 12 9. 17	144.52
1972	321.16	348.95		257.16	316,88	219.99	0	226.77	296.78	363.54	227.72
1974	300.21	363.95		291.33	318.41	295.56	ő	317.05	328.16	252.62	299.55
1975	236.89	349.97		271.48	286.03	256.07	ő	368.11	0	452.10	284.62
1976	267.63	372.46		253.76	307.45	292.15	ő	367.73	Õ	452.10	312.31
1977	338.29	409.01		318.00	349.32	333.34	Õ	337.06	ő	338.45	335.14

		STAT	E OF OREGON ¹			NORTHERN CALIFORNIA						
YEAR AND QUARTER	ASTORIA	COOS BAY	PORTLAND	OTHER	AVERAGE	EUREKA	REDWOOD CITY	SACRAMENTO	STOCKTON	OTHER	AVERAGE	
1970	121.59	199.84	128.71		142.46	111.22	90.00	114.04	96.95	92.28	109,81	
1971	117.61	212.89	126.33		140.64	107.55	126.58	110.37		0	108.76	
1972	127.03	194.93	144.27	140.31	147.35	129.24		189.29	179.64	129.17	144.52	
1973	321 .1 6	348.95	289.64	257.16	316.88	219.99	0	226.77	296.78	363.54	227.72	
1974	300.21	363.95	302.18	291.33	318.41	295.56	0	317.05	328.16	252.62	299.55	
1975	236.89	349.97	316.25	271.48	286.03	256.07	0	368.11	Q	452.10	284.62	
1976	267.63	372.46	337.44	253.76	307.45	292.15	Ō	367.73	0		312.31	
1977	338.29	409.01	328.22	318.00	349.32	333.34	0	337.06	0	338.45	335.14	
1978	325.32	512.44	366.77	330,78	389.23	353.99	0	362.18		372.07	358.09	
1979 1980	461.34	592.98	455.51	381.59	483.38	336.29	0	393.19		447,84	369.65	
1st quarter	477.16	631.94	501.19	0	531.66	439.82	0	0	379.65	495.42	458,30	
2d quarter	521.89	631.10	503.85	ŏ	536.72	531.32	ŏ	ŏ	0	895.65	551.48	
3d quarter	405.84	590.80	495.56	ō	495.87	397.75	ŏ	ő	ŏ	535.94	489.40	
4th quarter	386.99	540.59	447.85	0	455.45	505.15	ō	485.28	Ö	608.07	503.48	
1980 average	452.99	604.08	488.22	0	508.23	462.98	0	485.28	379.65	535.17	492.37	
1981 1st guarter	356.89	683.24	426.13	0	479.01	0	0	521.81	0	986.26	539.15	
2d quarter 3d quarter 4th quarter												
1981 average												

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

¹State averages as presented here for Washington and Oregon do not agree with those found in table 10 because customs districts as used in table 10 do not correspond to State boundaries.

YEAR AND QUARTER	VOLUME	AVERAGE VALUE
	TO ALL COUNTRIES	
1970	51,531	125.58
1971	42,600 65,837	116.54 125.88
1972 1973	71,719	248.23
1974	34,949	240.82
1975	29,011	307.97
1976 1977	26,197 52,377	224.59 263.54
1978	68,025	320.45
1979	128,597	470.97
1980 1st quarter	26,021	475.33
2d quarter	44,334	501.91
3d quarter	44,334 58,369	537.30
4th quarter	31,799	613.44
1980 total and average value	160,523	532.56
1981 1st quarter	25,305	584.21
2d quarter 3d quarter 4th quarter		
1981 total and average value		
	TO JAPAN	
1970	47,583 38,948	129.67
1971 1972	38,948 61,882	120.94 129.99
1973	71.705	248.24
1974	29,088	252.71
1975	24,311	352.29
1976 1977	20,741 46,897	253.18 278.99
1978	57,653	343.49
1979	120,753	475.21
1980 Ist quarter	25,223	472.33
2d quarter	42,239	512.10
3d quarter	57,678	535.22
4th quarter	31,135	607.49
1980 total and average value	156,275	533.22
1981 1st quarter 2d quarter	24,979	507,25
3d quarter 4th quarter		
1981 total and average value		
	TO MAINLAND CHINA	
1981	162	251 20
1st quarter 2d quarter 3d quarter	163	351.39
4th quarter		
1981 total and average value		

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Uata are compiled from Department of Commerce records at the end of each quarter.

			-	O ALL COUNTRI	ES			
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980	2,052 786 2,999 1,812 633 1,599 3,750 2,735 2,362 2,597	921,655 681,962 882,806 1,351,759 1,121,199 637,455 1,646,972 2,117,386 2,190,449 2,216,256	98 192 68 36 45 73 236 189 75 341	78,348 245,213 133,979 57,747 95,342 103,519 136,188 87,839 91,486 420,741	0 0 0 0 0 0 0 0 0 11 138	 19,250 253,716	2,353 1,275 1,320 1,084 560 3,911 659 1,396 1,772 1,272	2,973,898 1,643,951 2,015,855 2,330,761 1,515,476 780,853 1,239,777 2,751,996 4,088,466 3,049,981
1st quarter 2d quarter 3d quarter 4th quarter	2,918 1,914 1,194 800	1,336,275 1,173,664 1,494,397 1,149,375	327 909 142 648	94,704 351,476 66,189 252,142	28 78 74 6	7,000 23,200 10,000 4,760	249 390 52 209	757,307 808,759 101,932 592,963
1980 total	6,826	5,153,711	2,026	764,511	186	44,960	900	2,260,961
1981 Ist quarter 2d quarter 3d quarter 4th quarter	1,250	969,546	122	162,848	0		404	834,877
1981 total								
	J-1000			TO JAPAN				
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	1,672 762 1,374 993 540 1,210 3,313 1,444 1,178 1,824	889,649 669,251 727,475 1,164,704 1,063,245 562,583 1,416,317 1,179,616 819,332 1,153,644	96 192 64 34 37 14 235 17 57 300	75,855 245,213 130,080 56,842 84,293 9,039 134,988 33,347 84,025 359,119	0 0 0 0 0 0 0 0	 188,389	2,296 1,222 1,126 1,015 485 3,803 456 1,063 1,248 1,069	2,935,506 1,588,353 1,761,797 2,250,213 1,093,502 636,796 1,005,649 2,300,667 3,059,204 2,339,089
1980 1st quarter 2d quarter 3d quarter 4th quarter	2,714 1,552 149 371	826,696 749,394 113,210 279,945	316 906 134 608	87,867 344,457 57,889 236,678	28 78 74 2	7,000 23,200 10,000 2,000	182 206 51 140	602,583 468,706 100,732 360,475
1980 total	4,786	1,969,245	1,964	726,891	182	42,200	579	1,532,496
1981 1st quarter 2d quarter 3d quarter 4th quarter	287	393,303	117	146,848	0		224	574,714
1981 total								
			<u></u>	O MAINLAND CH	INA			
1980— 1st quarter 2d quarter 3d quarter 4th quarter	 6 	2,800	 		 	 ,		
1980 total	6	2,800						
1981 1st quarter 2d quarter 3d quarter 4th quarter	0		o		0		0	
1981 total								

Source—U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Data are compiled from Department of Commerce records at the end of each quarter. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Alaska Customs District is the State of Alaska. San Francisco Customs District includes Monterey and all ports north of Monterey, California.

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	HAR DWOODS
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	561 365 631 445 378 288 2,396 1,360 1,721 2,117	276 90 203 214 32 11 1,411 169 172 290	60 84 92 5 130 224 670 411 917 359	225 191 336 226 216 53 315 780 632 1,468
1st quarter 2d quarter 3d quarter 4th quarter	232 376 406 135	59 171 65 0	98 110 303 99	75 95 38 36
1980 total	1,149	295	610	244
1981 1st quarter 2d quarter 3d quarter 4th quarter	235	30	86	119
1981 total				

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter. Revisions which may have been made after this time are not shown. Southern California consists of the San Diego and Los Angeles Customs Districts and includes all ports south of Monterey, California.

	ALL :	SPECIES	DOUGL	AS-FIR	OTHER S	OFTWOODS
YEAR AND QUARTER	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE
1970	96	111.47	30	146.57	66	95.62
1971	853	103.53	0		853	103.53
1972	392	113.71	19	162.89	373	111.20
1973	379	177.58	93	261.16	286	150.40
1974	925	178.24	19	149.05	. 906	178.86
1975	739	226.93	72	274.78	667	221.76
1976	57 1	228.43	103	254.08	468	222.78
1977	1,227	247.66	467	251.10	760	245.54
1978	901	226.05	136	367.43	765	200.91
1979	3,906	168.47	0	***	3,906	168.47
1980			•			
1st quarter	135	303.18	15	281.67	120	305.87
2d quarter	236	189.98	0		236	189.98
3d quarter	156	257.12	21	319.14	135	247.47
4th quarter	172	243.02	0		172	243.02
1980 total and average value	699	239.88	36	303.53	663	236.42
1981— 1st quarter 2d quarter 3d quarter 4th quarter	141	446.81	123	475.06	18	253 . 78

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Data are compiled from Department of Commerce records at the end of each quarter.

1 Montana Customs District includes all ports in Montana and Idaho.

			TO ALI	COUNTRIES		· —	
1970 1971 1972 1973 1974 1975 1976 1977 1978	269,201 158,579 55,866 35,716 148,801 85,082 116,193 186,511 128,853 169,107	4,209 3,750 836 1,852 11,790 2,406 5,390 10,085 8,592 2,431	90,266 41,633 13,956 9,750 31,528 18,914 39,069 118,085 24,467 56,504	59,641 48,260 18,477 7,441 67,843 19,373 21,901 36,048 45,143 56,954	61,192 45,519 14,958 13,647 27,355 41,416 41,959 19,835 49,767 43,201	51,660 14,177 3,965 1,211 4,973 1,505 3,346 754 530 4,135	2,233 5,240 3,674 1,815 5,312 2,188 4,528 1,704 354 5,882
1980 1st quarter 2d quarter 3d quarter 4th quarter	41,753 45,863 94,870 49,298	0 6,177 1,687 1,043	14,899 14,830 52,201 24,263	11,096 6,688 19,681 12,125	9,341 9,950 11,246 6,219	1,864 3,482 6,676 133	4,553 4,736 3,379 5,515
1980 total	231,784	8,907	106,193	49,590	36,756	12,155	18,183
1981 1st quarter 2d quarter 3d quarter 4th quarter	NA	NA	NA	NA	NA	NA	NA
1981 total			TO) JAPAN			
1970 1971 1972 1973 1973 1974 1975 1976 1977 1978	148,502 94,669 46,059 29,239 80,655 61,728 67,192 109,301 90,001 120,297	2,833 2,218 567 1,293 2,167 1,460 792 5,106 4,094 1,894	39,338 21,362 13,478 8,058 22,968 10,477 17,026 65,092 16,890 49,281	30,100 24,150 13,412 6,205 31,915 7,696 7,343 23,413 24,038 27,597	54,642 40,472 14,938 13,284 16,503 39,470 39,905 15,489 44,814 35,883	21,479 6,379 3,664 399 2,304 1,253 470 201 99 3,636	110 88 0 0 4,798 1,372 1,656 0 66 2,056
1980 1st quarter 2d quarter 3d quarter 4th quarter	31,167 27,348 65,015 31,294	0 303 576 813	9,479 5,234 34,851 11,936	7,701 6,436 13,563 7,646	9,336 9,950 10,637 6,234	1,515 2,800 2,491 133	3,136 2,625 2,897 4,532
1980 total	154,824	1,692	61,500	35,346	36,157	6,939	13,190
1981 1st quarter 2d quarter 3d quarter 4th quarter	NA	ΝΛ	AA	NΛ	NA	NA	NA
1981 total							
			TO UN	ITED STATES			
1970 1971 1972 1973 1974 1975 1976 1977 1978	120,698 63,910 9,807 6,471 68,146 23,354 48,911 74,442 32,843 48,810	1,376 1,532 269 559 9,623 946 4,598 4,979 4,498 537	50,928 20,271 478 1,692 8,560 7,717 22,043 50,817 6,039 7,223	29,540 24,110 5,065 1,236 35,928 11,677 14,558 12,043 19,144 29,357	6,550 5,047 20 363 10,852 1,946 1,964 4,346 2,443 7,368	30,181 7,798 301 812 2,669 252 2,876 553 431 499	2,123 5,152 3,674 1,809 514 816 2,872 1,704 288 3,826
1980 1st quarter 2d quarter 3d quarter 4th quarter	10,581 18,515 29,770 18,089	0 5,874 1,111 230	5,420 9,596 17,350 12,327	3,395 252 6,048 4,549	0 0 594 0	349 682 4,185 0	1,417 2,111 482 983
1980 total	76,955	7,215	44,693	14,244	594	5,216	4,993
1981— 1st quarter 2d quarter 3d quarter 4th quarter	NA	NA	NA	NA	NA	NA	NA
1981 total							

Source--Bureau of Economics and Statistics, Department of Industrial Development, Trade, and Commerce, Victoria, B.C., "Preliminary Statement of External Trade."

¹Figures do not include shipments of pulpwood logs.

NA = not available.

YEAR AND QUARTER	VOL UME	AVERAGE VALUE
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	99,462 60,333 8,451 2,102 31,625 55,494 44,438 91,962 41,307 75,855 9,115 8,377 15,486 18,850	82.57 64.70 80.44 124.71 248.69 207.13 122.62 194.93 271.29 298.89 341.27 319.09 233.34 142.33
1980 total and average value 1981— 1st quarter 2d quarter 3d quarter 4th quarter	51,828 13,223	233.08
1981 total and average value		All Printed and Market Street Street (1994), and a second second second second second second second second sec

Source—U.S. Department of Commerce. Value is declared value at port of entry. Data are compiled from Department of Commerce records at the end of each quarter.

	CHIPPED F	OLFWOOD	KOUNDWOOL	POLPWOOD
YEAR AND QUARTER	VOLUME	VALUE	VOLUME	VALUE
	Short tons	Dollars	Cords	Dollars
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	795,044 1,157,444 909,926 1,085,124 623,830 493,761 877,550 1,056,102 1,215,483 1,039,458 252,549 375,769 264,794 292,589	8.44 9.57 9.87 11.19 15.55 23.36 20.98 18.59 16.37 17.19 23.92 24.76 27.28 31.36	17,501 3,944 2,300 16 31,998 11,517 1,967 16,674 150 5,182 5,638 46,367	NA 19.47 47.56 97.06 60.08 42.90 32.14 91.19 86.87 125.75 165.90 47.,0
1980 total and average value 1981 1st quarter 2d quarter 3d quarter	1,185,701 318,965	26.77 33.14	57,337 13,245	66.64 134.14

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

NA = not available.

		HINGION S DISTRICT	OREC CUSTOMS [RANCISCO DISTRICT		SKA DISTRICT
YEAR AND QUARTER	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUMÉ	VALUE
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980— 1st quarter 2d quarter 3d quarter 4th quarter	238,757 229,237 168,725 272,196 390,370 326,083 457,801 281,540 299,140 346,209 21,508 123,993 31,697 90,905	19.56 17.87 19.56 21.84 28.62 38.56 33.39 49.17 46.16 50.05 56.29 76.67 91.79 84.65	1,605,062 1,504,169 2,081,032 2,778,829 3,177,465 2,436,807 2,881,577 2,882,333 2,550,423 3,125,103 737,661 767,411 716,415 628,440	19.31 20.94 22.12 24.85 26.50 34.74 39.90 43.33 42.98 42.55 63.71 85.88 109.10 97.05	267,347 476,400 253,401 369,403 242,017 257,735 366,678 519,444 412,107 603,989 134,188 236,482 214,926 142,863	NA NA 27.76 24.41 30.69 28.96 34.76 42.91 40.82 44.69 63.84 66.31 114.01 96.28	19,600 20,158 34,828 32,399 107,652 107,429 31,827 83,706 30,649 57,860 40,103 22,716	28.06 25.76 28.99 48.51 37.89 51.67 37.20 48.62 83.49 49.94 97.34 91.76
1980 total and average value 1981 1st quarter 2d quarter 3d quarter 4th quarter	268,103 49,140	79.53 73.54	2,849,927 715,962	88.44 87.17	728,459 136,498	85.81 91.69	151,328 10,534	75.57 48.05
1981 total and average value								

Source—U.S. Department of Commerce except for San Francisco data for 1970 and 1971 which were obtained from the Port of Sacramento. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Washington Customs District includes all ports in the State of Washington, except Longview and Vancouver. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. San Francisco Customs District includes all coastal and inland ports in the State of California from Monterey north. The Alaska Customs District is the State of Alaska.

NA = not available.

981— Ist quarter 2d quarter 3d quarter 4th quarter	441	359	0	82	82	0	0	82	359	359	0	
					IAM OT	NLAND CHINA	1					
1981 total					<u></u>							
981— 1st quarter 2d quarter 3d quarter 4th quarter	51,382	20,608	4,922	25,852	51,382	20,608	4,922	25,852	0	0	0	
1980 total	159,658	54,876	26,325	78,457	159,658	54,876	26,325	78,457	0	0	0	
lst quarter 2d quarter 3d quarter 1th quarter	46,038 47,329 30,018 36,273	16,609 17,946 8,851 11,470	10,231 6,469 3,979 5,646	19,198 22,914 17,188 19,157	46,038 47,329 30,018 36,273	16,609 17,946 8,851 11,470	10,231 6,469 3,979 5,646	19,198 22,914 17,188 19,157	0 0 0	0 0 0 0	0 0 0 0	
170 171 172 173 174 175 176 177 178 179	44,153 46,618 70,297 88,695 126,547 113,213 101,633 76,251 117,969 113,977	32,029 32,989 42,581 49,381 67,856 61,099 50,327 45,842 69,852 38,917	1,384 1,339 8,687 9,340 5,952 4,299 6,737 3,695 9,241 18,870	10,740 12,290 19,029 29,974 52,739 47,815 44,569 26,714 38,876 56,190	44,153 46,618 70,297 88,695 124,097 112,783 101,633 76,251 117,930 113,977	32,029 32,989 42,581 49,381 65,406 61,099 50,327 45,842 69,813 38,917	1,384 1,339 8,687 9,340 5,952 3,869 6,737 3,695 9,241 18,870	10,740 12,290 19,029 29,974 52,739 47,815 44,569 26,714 38,876 56,190	0 0 0 0 2,450 430 0 0 39	0 0 0 0 2,450 0 0 0 39	0 0 0 0 430 0 0	
					·	CANADA		10.740				
1981 total												********
81 st quarter d quarter d quarter th quarter	82,390	17,199	51,779	13,412	55,324	9,201	36,658	9,465	27,066	7,998	15,121	3,9
980 total	362,458	53,084	249,729	59,645	269,406	26,428	199,237	43,741	93,052	26,656	50,492	15,9
st quarter d quarter d quarter th quarter	89,497 117,162 88,436 67,363	10,144 17,324 16,380 9,236	61,733 81,874 58,701 47,421	17,620 17,964 13,355 10,706	70,326 82,103 62,808 54,169	5,917 7,042 7,793 5,676	53,218 62,243 44,347 39,429	11,191 12,818 10,668 9,064	19,171 35,059 25,628 13,194	4,227 10,282R 8,587 3,560	8,515 19,631 14,354 7,992	6,4 5,1 2,6 1,6
75 76 77 78 79 80	145,386 163,233 355,840	102,858 96,307 68,927 40,945 36,429 75,567	99,707 77,973 96,610 107,884 93,719 108,610 227,702		258,444	45,549	47,616 45,359 80,891 80,161 103,056 177,239	11,491 3,139 7,232 7,462 13,289 35,656	21,270 97,396	58,434 55,316 29,497 20,100 10,820 30,018	30,357 51,251 26,993 13,558 5,554 50,463	8,1 13,5 12,1 2,5 3,2 4,8 16,9
70 71 72 73 74	30,294 16,736 23,699 153,537 205,888 208,160	4,949 3,252 3,437 40,402 102,858	14,983 7,080 10,589 99,707 77,973	10,362 6,404 9,673 13,428 25,057 15,243 9,817 10,722 18,194 52,571	13,859 12,816 14,951 89,514 103,531 89,489 127,553 108,468	2,656 2,239 571 19,247 44,424 40,991 39,430 20,845	5,693 5,610 7,291 64,966 47,616	5,510 4,967 7,089 5,301 11,491	16,435 3,920 8,748 64,023 102,357 118,671 59,075	2,293 1,013 2,866 21,155 58,434	9,290 1,470 3,298 34,741 30,357	4,8 1,4 2,5 8,1
					TO) JAPAN						
d quarter d quarter th quarter 981 total				· t · · · · · · · ·								***********
980 total 81 st quarter	984,882 245,806	449,123 124,627	338,487 68,610	197,272 52,569	521,728 125,778	106,671 35,531	270,706 50,166	144,351 40,081	463,154 120,028	342,452 89,096	67,781	12,4
d quarter d quarter th quarter	247,234 312,038 217,915 207,695	113,090 146,872 95,562 93,599	89,573 106,431 75,976 66,507	44,571 58,735 46,377 47,589	159,134 111,680 110,091	32,973 22,074 23,306	81,467 57,714 55,041	44,694 31,892 31,744	152,904 106,235 97,604	113,899 73,488 70,293	24,964 18,262 11,466	8,5 14,0 14,4 15,8
77 78 79 30 st quarter	698,941 549,059 585,588 839,895	372,609 374,032 427,063	125,479 135,156 280,067	50,971 76,400 132,765	256,703 310,100 413,673	123,783 128,895 98,685	92,364 118,094 211,030	40,556 63,111 103,858 36,021	292,356 275,488 426,322	248,826 245,137 328,378 84,772	33,115 17,062 69,031	10,4 13,2 28,9
70 71 72 73 74 75	409,872 334,318 406,493 799,631 719,729 616,883 698,941	304,578 267,429 321,761 532,321 496,978 415,152 478,100	33,810 22,344 30,772 169,927 124,047 125,529 145,645	44,545 53,960 97,383 98,704 76,202 75,196	130,186 164,472 324,740 331,818 263,754 311,599	88,532 99,927 143,666 174,056 151,681 155,041	12,279 9,902 21,994 104,851 79,399 52,064 94,581	47,444 31,752 42,551 76,223 78,363 60,009 61,977	273,748 204,132 242,021 474,891 387,911 353,129 387,342	178,897 221,834 388,655 322,922 263,471 323,059	12,442 8,778 65,076 44,648 73,465 51,064	24,0 12,7 11,4 21,1 20,3 16,1 13,2
				71,484	136,124	76,401				228,177	21,531	

		TO ALL COUNTRIES		
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	52,681 38,397 48,914 73,842 35,314 27,628 40,585 44,438 32,919 30,832 7,934 13,118 6,983 6,568	26,645 21,267 20,843 30,746 17,350 13,388 14,430 18,951 12,931 10,539 1,780 6,385 1,167 1,199	8 0 135 2,530 815 636 462 1,137 684 1,498 354 849 1,360 1,214	26,028 17,130 27,936 40,566 17,149 13,604 25,693 24,350 19,304 18,795 5,800 5,884 4,456 4,155
1980 total	34,603	10,531	3,777	20,295
1981 1st quarter 2d guarter 3d quarter 4th quarter	7,446	2,183	2,002	3,261
1981 total				
		TO JAPAN		
1970 1971 1972 1973 1974 1975 1976 1977 1978	8,472 3,695 6,884 4,963 3,208 4,303 5,724 7,766 6,763 8,854	48 0 17 328 317 337 168 1,354 107	0 28 2,359 12 396 200 700	8,424 3,695 6,839 2,276 2,879 3,966 5,160 6,412 6,456 8,154
1980 1st quarter 2d quarter 3d quarter 4th quarter	4,173 4,188 4,431 4,592	58 306 574 222	274 716 1,052 1,214	3,841 3,166 2,805 3,156
1980 total	17,384	1,160	3,256	12,968
1981 1st quarter 2d quarter 3d quarter 4th quarter	4,520	464	1,809	2,247
1981 total				

Source--U.S. Department of Commerce.

 $^{^{1}}$ Northern California consists of the San Francisco Customs District and includes Monterey, California, and all ports north of Monterey.

YEAK AND QUAKTER	TUTAL	DOUGLAS-FIR	20F LMOON2
	TO ALL	COUNTRIES	
1970	45,405	18,751	26,654
1971	42,446	15,086	27,360
1972	56,599	23,938	32,661
1973	52,608	19,599	33,009
1974	46,514 56,759	18,684 23,596	27,830 33 163
1975 1976	61,256	23,078	33,163 38,178
1977	72,588	26,895	45,693
1978	74,347	27,661	46,686
1979	81,372	20,388	60,984
1980	17 551	2 070	12 501
1st quarter	17,551 25,062	3,970 6,220	13,581 18,842
2d quarter 3d quarter	25,754	6,251	19,503
4th quarter	27,274	8,389	18,885
Ton quarter		-,000	
1980 total	95,641	24,830	70,811
1981			
1st quarter	24,137	5,252	18,885
2d quarter			
3d quarter			
4th quarter			
1981 total			
	ТО	JAPAN	
1970		deta has	
1971	1,156		1,156
1972	1,578	12	1,566
1973	264		264
1974 1975	64 119		64 119
1976	377		377
1977	172	73	99
1978	471		471
1979	739		739
1980	100		100
1st quarter	180	20	180
2d quarter 3d quarter	284 760	20	264 760
4th quarter	1,106	217	889
quui voi		• • •	
1980 total	2,330	237	2,093
1981			
1st quarter	490	68	422
2d quarter			
3d quarter 4th quarter			•
ion quarter		· · · · · · · · · · · · · · · · · · ·	

Source—U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

 $^{1}\mathrm{Southern}$ California consists of the San Diego and Los Angeles Customs Districts and includes all ports south of Monterey, California.

1981 total

QUINTER	TOTAL	HEHEOOK	31 KOGC	OLD/III	301 1NOO0.
		TO ALL COU	NTRIES		
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	315,586 247,414 340,196 404,849 362,432 313,307 290,011 250,044 237,795 278,462 256,716 66,402 84,526 58,537 47,251	90,974 92,243 155,407 210,555 250,144 179,398 134,387 122,544 126,218 172,005 158,682 43,514 52,75 33,638 28,778	219,001 155,171 184,649 194,143 154,525 132,556 148,526 121,350 111,435 103,844 96,607 22,888 31,669 24,221 17,829	708 0 0 12 2,641 1,353 1,298 5,579 53 479 105 0 105 0	4,893 0 140 139 122 0 5,800 571 89 2,134 1,322 0 678 644
1980 total	256,716	158,682	96,607	105	1,322
1981— 1st quarter 2d quarter 3d quarter 4th quarter	54,446	22,644	31,802	0	0
1981 total					
		TO JAP	N		
1970 1971 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	315,386 245,974 336,798 403,938 361,691 312,976 289,197 245,445 236,615 273,615 251,369 63,403 84,505 56,854 46,607	90,774 91,357 152,555 210,536 204,845 179,122 134,274 122,471 125,355 170,149 156,654 41,507 52,731 33,638 28,778	219,011 154,617 184,243 193,390 154,205 132,501 148,221 121,083 111,207 101,408 94,610 21,896 31,669 23,216 17,829	708 0 0 12 2,641 1,353 902 1,391 53 435 105 0 105 0	4,893 0 0 0 0 0 5,800 500 0 1,623 0 0
1980 total	251,369	156,654	94,610	105	0
1981— 1st quarter 2d quarter 3d quarter 4th quarter	41,731	18,861	22,870	0	0
1981 total					
		TO MAINLAND	CHINA		
1981— 1st quarter 2d quarter 3d quarter 4th quarter	8,721	0	8,721	0	0
1981 total					

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of \boldsymbol{e} ach quarter.

				
YEAR AND QUARTER	TOTAL	DOUGLAS-FIR	WESTERN HEMLOCK	OTHER SOFTWOODS
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter	10,794 12,417 16,360 47,727 29,146 50,226 56,451 46,488 44,612 81,671	6,424 4,660 6,391 30,526 9,618 12,745 19,050 12,660 12,691 22,067	32 800 1,595 3,334 3,602 4,516 3,521 3,463 2,276 1,632	4,338 6,957 8,374 13,867 15,926 32,965 33,880 30,365 29,645 57,972
2d quarter 3d quarter 4th quarter	14,497 12,692 11,909	4,434 3,099 2,848	303 650 583	9,760 8,943 8,478
1980 total	57 , 556	14,030	1,803	41,723
1981 1st quarter 2d quarter 3d quarter 4th quarter	19,012	3,036	298	12,678
1981 total				

Source--U.S. Department of Commerce.

 $^{{}^{1}\}mathrm{Montana}$ Customs District includes all ports in Montana and Idaho.

991 1,300,365 67,773 1,703,632 322,400 440,555 153,769 1,686 3793 1,824,555 70,112 1,801,818 405,609 63,453 27,453 1,814,355 170,112 1,801,818 405,609 63,453 27,453 1,814,355 170,112 1,801,818 405,609 63,453 27,453 1,814,359 1,914,781 387,043 1,914,781 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 387,043 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 4,914,781 1,914,781 1,914,781 4,914,781 1,9				TO ALL COUNTR	IES			
1977	1970 1971 1972 1973 1974 1975	3,300,365 3,834,552 4,169,812 3,938,940 3,001,410	707,112 566,535 527,706 356,371	1,703,632 1,801,818 2,032,594 1,699,277 1,113,665	324,910 406,409 456,522 406,419	440,595 634,563 766,830 914,787 825,527	153,769 278,836 344,401 387,043 409,507	2,129 1,686 5,814 2,930 3,708 1,122
36 quarter 1,348,985 111,005 495,664 135,901 402,394 21,097 1,385 11,005 495,664 135,901 465,075 21,097 31,623 1,385 11,385 115 quarter 21 quarter 31 40 40 40 40 40 40 40 40 40 40 40 40 40	977 978 979	5,860,807 5,876,119	683,614 679,566	2,492,764 2,313,186	533,267 570,796	2,269,876 2,116,258	8,796 15,674	1,279 1,226 1,061 2,961
981 1st quarter	2d quarter 3d quarter	1,647,910 1,348,984	118,785 155,116	487,292	462,851 218,542	498.880 462,354	22,988 24,691	369 989
1st quarter 2d quarter 3d quarter 590,986 283,482 775,427 355,819 1,079,387 94,683 2,088 497 1,131 990 305,289 970 3,580,680 3,780 305,380 3	1980 total	5,560,800	498,425	2,098,672	988,347	1,872,234	99,624	3,498
970 727,599 29,489 549,584 94,820 53,725 2 0 971 419,819 14,181 305,535 44,221 54,136 1,668 78 972 400,051 15,268 300,460 46,052 34,003 526 3,742 973 617,449 12,987 441,852 88,946 71,531 ,849 284 974 500,785 15,335 349,660 83,749 49,116 2,490 535 975 407,674 12,870 301,336 60,490 30,488 2,405 85 976 633,863 13,727 476,927 79,934 61,743 1,521 11 977 705,823 18,530 530,567 90,447 66,943 85 978 779,135 23,799 545,963 116,366 92,940 0 45 978 779,135 23,799 545,963 116,366 92,940 0 45 979 1,014,461 40,021 67,725 186,121 133,358 66 1,001 184 quarter 311,989 15,219 190,571 46,185 51,682 273 59 36 quarter 311,989 15,219 190,571 46,185 51,682 273 59 36 quarter 193,192 12,184 133,325 7,931 35,563 2,688 891 1980 total 1,084,426 55,800 701,579 136,130 185,379 4,156 1,360 991 12,163,431 502,631 1,028,356 203,577 285,343 141,943 1,591 1972 24 quarter 34 quarter 35 quarter 34 quarter 35 quarter 34 quarter 34 quarter 34 quarter 37 quarter 38 quarter 38 quarter 39 quarte	Ist quarter 2d quarter 3d quarter	NA	NA	NA	NA	АН	NA	NA
970 727,599 29,489 549,554 94,828 53,726 2 0 971 419,819 14,181 305,555 44,221 54,136 1.668 78 972 400,051 15,268 300,460 46,052 34,003 526 3,742 973 500,785 15,355 349,566 63,749 17,1531 18 2,490 535 974 500,785 15,355 349,566 63,749 34,181 2,490 535 975 500,785 15,355 349,566 63,749 34,181 2,490 535 976 633,653 13,727 476,927 79,330 61,743 1,521 117 977 705,823 18,530 530,567 90,447 65,943 16,221 17,97 978 779,135 23,799 545,993 116,366 92,940 0 64,999 116,494 17,998 17,913 12,21 111,999 116,360 17,43 11,221 111,997 151 quarter 286,101 10,072 184,803 46,699 43,556 660 320 24 quarter 311,999 15,219 190,571 46,185 51,662 273 59 34 quarter 133,325 184,280 35,324 54,578 577 110 970 1,627,613 401,167 768,772 137,361 202,152 116,032 2,129 190 571 46,185 74,782 577 110 981— 151 quarter 281,199 15,219 190,571 46,185 51,662 273 59 34 quarter 133,192 12,184 133,325 104,280 35,324 54,578 577 110 1980 total 1,084,426 55,800 701,579 136,130 185,379 4,158 1,380 981— 151 quarter 30 40,426 55,800 701,579 136,130 185,379 4,158 1,380 981— 151 quarter 30 40,426 55,800 701,579 136,130 185,379 4,158 1,380 981— 151 quarter 30 40,426 55,800 701,579 136,130 185,379 4,158 1,380 981— 151 quarter 40 40 40 40 40 40 40 40 40 40 40 40 40	1981 total							
971				TO JAPAN				
1,014,401 10,072 184,803 46,690 43,556 660 320 320 320 340 340,890 31,989 15,219 190,571 46,185 51,682 273 59 36 quarter 293,144 18,325 184,280 35,324 54,578 527 110 4th quarter 193,192 12,188 133,925 7,931 35,563 2,698 891 1980 total 1,084,426 55,800 701,579 136,130 185,379 4,158 1,380 981—	971 972 973 974 975 976	419,819 400,051 617,449 500,785 407,674 633,863	14,181 15,268 12,987 15,335 12,870 13,727	305,535 300,460 441,852 349,560 301,336 476,927	44,221 46,052 88,946 83,749 60,490 79,934	54,136 34,003 71,531 49,116	1,668 526 1,849 2,490 2,405 1,521	78 3,742 284 535 85 11
2d quarter 311,989 15,219 190,571 46,185 51,682 273 59 3d quarter 293,144 18,325 184,280 35,324 54,578 527 110 4th quarter 193,192 12,184 133,925 7,931 35,563 2,698 891 1980 total 1,084,426 55,800 701,579 136,130 185,379 4,158 1,380 981— 1st quarter NA	.978 .979	779,135 1,014,481	23,799	545,983	116,368 158,121	92,940 133,358	0	45
981— 1st quarter	2d quarter 3d quarter	286,101 311,989 293,144 193,192	15,219	198,571 184,280	46,185	51,682 54,578	273 527	59 110
1981 total TO UNITED STATES1 TO UNITED STATES1 TO UNITED STATES1 970		1,084,425	55,800	701,579	136,130	185,379	4,158	1,380
970	1st quarter 2d quarter 3d quarter	NA	NA	NA	NA	NA	NA	NA
1,627,613	1981 total							
9/3				TO UNITED STA	TES ¹			
1st quarter 637,007 58,070 217,757 96,434 244,783 19,544 419 2d quarter 609,9325 58,994 166,082 93,966E 267,947 22,636 307 3d quarter 591,133E 98,469 138,128 69,453E 260,570 23,645 868 4th quarter 752,814 67,949 253,460 95,966 306,087 28,858 494 1980 total 2,590,886 283,482 775,427 355,819 1,079,387 94,683 2,088 981— 1st quarter NA	971 972 973 974 975 976 977 978 979	2,163,431 2,679,159 2,601,556 2,287,461 2,026,343 2,965,011 4,107,653 4,078,666	502,631 505,902 347,653 302,112 238,331 322,793 529,808 501,841	1,028,356 1,155,419 1,143,329 761,924 542,256 978,784 1,340,920 1,443,548	254,521 240,978 207,138 166,949 267,831 333,604 365,062	544,634 659,751 684,404 938,185 1,894,371 1,751,741	141,943 270,029 322,316 353,487 393,391 456,237 7,988 15,496	1,581 2,071 2,646 3,049 1,012 1,181 962 978
981—	1st quarter 2d quarter 3d quarter	609,932E 591,133E	58,994 98,469	166,082 138,128	93,966E 69,453E	267,947 260,570	22,636 23,645	307 868
1st quarter NA NA NA NA NA NA NA NA 2d quarter 3d quarter		2,590,886	283,482	775,427	355,819	1,079,387	94,683	2,088
	1st quarter 2d quarter 3d quarter	NA	NA	АИ	AM	NA	NA	NA

Source—Bureau of Economics and Statistics, Department of Industrial Development, Trade, and Commerce, Victoria, B.C., "Preliminary Statement of External Trade."

 $¹_{\mbox{\it Figures}}$ do not include shipments of railroad crossties.

E ≠ estimated.

NA = not available.

	COSTOMS	DISTRICTS	CUSTOMS D	TSTRICTS	CUSTOMS D	ISTRICTS
YEAR AND QUARTER	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE
		TO A	LL COUNTRIES			-
1970 1971 1972 1973 1974 1975 1976	89,946 71,479 122,242 284,806 284,487 407,117 532,576	887 1,314 3,603 6,337 6,590 10,493 24,229	10,587 11,247 23,241 45,493 131,317 93,951 34,020	812 1,035 3,342 5,546 5,604 10,360 23,846	79,359 60,232 99,001 239,313 153,170 313,166 498,556	75 279 261 791 986 133 383
1977 1978 1979 1980	233,762 242,105 330,018	17,673 12,160 9,962	20,603 23,284 27,132	17,447 8,871 9,644	213,159 218,821 302,886	226 3,289 318
1st quarter 2d quarter 3d quarter 4th quarter	89,009 100,285 40,098 49,611	2,786 3,164 2,356 1,412	3,445 8,686 3,916 4,700	2,066 3,078 2,304 1,358	85,564 91,599 36,182 44,911	720 86 52 54
1980 tota1	279,003	9,718	20,747	8,806	258,256	912
1981— 1st quarter 2d quarter 3d quarter 4th quarter	90,409	2,824	8,391	2,566	82,018	258
1981 tota1	Amerika da kajda ngaya spika ngaya ya mang Madi Mada kan Agua					
			TO JAPAN	-		
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980	998 1,369 734 8,139 3,311 2,141 2,361 1,914 2,821 6,040	2 28 34 247 188 14 61 162 18	525 633 432 1,625 1,203 414 498 122 167 931	2 28 0 0 11 0 61 74 18 108	473 736 302 6,514 2,108 1,727 1,863 1,792 2,654 5,109	0 0 34 247 177 14 0 88 0
1st quarter 2d quarter 3d quarter 4th quarter	838 5,134 1,386 943	4 85 889 0	270 3,158 443 287	4 85 889 0	568 1,976 943 656	0 0 0
1980 total	8,301	978	4,158	978	4,143	0
1981 1st quarter 2d quarter 3d quarter 4th quarter	1,294	4	581	3	713	1
1981 total						

Source--U.S. Department of Commerce. Oregon Customs District includes all Oregon ports plus Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

NORTHERN CALIFORNIA

YEAR AND QUARTER	TOTAL	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	8,593 11,440 15,429 16,562 18,177 19,619 19,696 9,198 6,036 5,934 1,678 2,426 2,260 2,690	4,338 4,303 6,633 8,186 4,985 7,874 10,085 5,148 2,833 1,638 384 261 279 490	373 139 668 698 305 542 92 646 899 871 208 71 477 93	3,231 5,896 5,941 4,358 7,978 6,311 4,681 1,818 964 1,946 591 1,169 779 1,007	651 1,102 2,187 3,320 4,909 4,892 5,111 1,586 1,340 1,479 495 925 725 1,100
1980 total	9,054	1,414	849	3,546	3,245
1981 1st quarter 2d quarter 3d quarter 4th quarter	1,811	463	114	433	801

1981 total

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter. Revisions which may have been made after this time are not shown. Northern California is the San Francisco Customs District and includes all coastal and inland ports from Monterey north. Southern California consists of the San Diego and Los Angeles Customs Districts and includes all ports south of Monterey, California.

AGENCY	1976	1977	1978	1979	TOTAL	1ST QTR.	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.	TOTAL.
Western Washington: U.S. Forest Service <u>l</u> / U.S. Bur. Indian Affairs State of Washington <u>2</u> /	883,213 18,300 690,015	1,066,656 17,036 746,012	1,097,548 66,923 175,155	22,882	1,114,024 6,927 503,565	217,198 4,673 248,970	202,579 0 115,505				
Total	1,591,528	1,829,764	1,339,675	2,396,365	1,624,516	470,841	318,084				
Eastern Washington: U.S. Forest Service1/ U.S. Bur. Land Manage. U.S. Bur. Indian Affairs State of Washington2/	247,937 3,058 351,112 82,138	271,698 2,768 301,161 82,828	382,902 54 157,396 30,385	420,819 2,645 140,247 125,505	428,631 1,798 211,205 80,345	92,031 0 59,022 38,665	63,187 0 18,403 9,480				
Total	684,245	658,455	570,737	689,216	721,979	189,718	91,070				
Western Oregon: U.S. Forest Service ¹ / U.S. Bur. Land Manage. State of Oregon		2,212,654 1,129,753 221,030		2,441,324 889,797 219,378		936,343 292,004 28,850	787,221 306,784 67,111				
Total	2,816,712	3,563,437	3,563,159	3,550,499	4,032,673	1,257,197	1,161,116				
Eastern Oregon: U.S. Forest Service1/ U.S. Bur. Land Manage. U.S. Bur. Indian Affairs State of Oregon	896,293 3,864 96,063	1,127,107 11,788 110,148 880	1,115,280 12,152 152,320 8,379	1,271,677 6,525 15,439 7,499	1,168,327 2,301 25,480 5,992	306,828 415 0	309,238 8 0 1,040		·		
- Total	996,220	1,249,923	1,288,131	1,301,140	1,202,100	307,243	310,286				
All public lands: U.S. Forest Service½/ U.S. Bur. Land Manage. U.S. Bur. Indian Affairs State of Washington½/ State of Oregon	3,627,754 1,028,199 465,475 772,153 195,124		4,838,134 1,122,657 376,639 205,540 218,732	5,356,368 898,967 178,568 1,276,440 226,877	5,354,698 1,154,125 243,612 583,910 244,923	1,552,400 292,419 63,695 287,635 28,850	1,362,225 306,792 18,403 124,985 68,151				
- Total	6,088,705	7,301,579	6,761,702	7,937,220	7,581,268	2,224,999	1,880,556				

Source--respective agencies listed.

 $^{{}^{1}\}text{Convertible products only.}$

 $²_{\mbox{Excludes}}$ sales under \$2,000.

AGENC I	1970	19//	1976	19/9	AVENAGE	121 614.	131 Qm.	LD QIN.	יעול מכ	אווי עות. אינאאטנ
Western Washington: U.S. Forest Servicel/ U.S. Bur. Indian Affairs State of Washington2/	93.54 120.88 159.27	106.12 163.54 159.89	129.57 120.34 231.31	224.68 264.95 332.10	208.06 182.32 304.71	232.76 211.07 349.71	235.69 0 234.09			
Average	122.35	128.58	142.84	276.66	237.91	294.38	235.11			
Eastern Washington: U.S. Forest Service1/ U.S. Bur. Land Manage. U.S. Bur. Indian Affairs State of Washington2/	39.45 69.71 79.81 101.19	56.36 77.02 91.74 107.39	186.69 123.48 165.37 162.13	104.68 16.80 212.01 210.79	90.92 21.25 162.32 207.67	115.07 182.27 211.16	64.56 159.70 276.21			
Average	67.71	79.10	179.49	145.50	124.63	155.56	105.78			
Western Oregon: U.S. Forest Service <u>l</u> / U.S. Bur. Land Manage. State of Oregon	141.54 157.74 146.11	181.51 180.82 172.37	210.96 196.36 226.23	332.09 292.59 314.93	354.60 323.63 332.25	384.23 353.50 308.35	358.34 309.79 315.67			
Average	147.73	180.73	207.31	321.13	344.44	375.35	343.05			
Eastern Oregon: U.S. Forest Service <u>l</u> / U.S. Bur. Land Manage. U.S. Bur. Indian Affairs State of Oregon	65.66 54.33 69.11	109.58 99.54 91.52 113.64	171.04 206.17 113.72 134.91	169.55 103.25 196.29 229.38	130.22 118.72 266.61 186.29	169.31 115.66	179.61 245.62 0 16.00			
Average	65.93	107.90	164.36	169.88	133.37	169.24	179.75			
All public lands: U.S. Forest Service1/ U.S. Bur. Land Manage. U.S. Bur. Indian Affairs State of Washington2/ State of Oregon	104.13 157.09 79.22 153.09 146.11	139.73 179.73 94.54 154.68 172.14	181.49 196.46 136.48 221.08 222.73	251.12 290.41 217.43 320.17 312.10	254.06 322.75 173.80 291.35 328.68	304.60 353.16 184.38 331.09 308.25	285.90 310.49 159.70 237.28 311.09			
Average	118.72	146.03	184.01	267.66	267.21	311.02	286.36			

Source--respective agencies listed.

1Prices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, quality, road costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stumpage prices include deposits for sale-area betterment.

²Excludes sales under \$2,000.

Table 32—Average stumpage prices for sawtimber sold on National Forests by selected species, Pacific Northwest Region, 1970-81¹ (In dollars per thousand board feet)

	DOUGLAS-FIR	S-FIR	PONDEROSA						1 1			NOBLE FIR	OTHE
YEAR AND QUARTER	WEST SIDE	EAST SIDE	AND JEFFREY PINES	SUGAR P I NE	WHITE PINE	LODGEPOLE PINE	ENGELMANN SPRUCE	SPRUCE	WESTERN HEMLOCK	CEDARS ²	LARCH	RED FIR	FIRS
							6	1 2	30.50	02 41	00 01	15 10	11.80
1970	41.90	8.40	20.30	30.00	37.30	4.20	3.90	07.11	20.00	14.70	10.30	27.10	12.20
1971	49.10	4.40	22.30	23.10	22.30	2.50	8.00	18.10	20.02	07.11	05.6	700.47	12.20
1972	71.70	15.60	38.40	26.00	35.80	10.60	27.20	28.00	49.00	67.50	13.50	100.20	33.00
1973	138.10	60.40	77.70	60.50	50.70	38.40	55.60	93.40	99.50	146.80	53.90	81.40	73.80
1974	202.40	68.20	110.60	139.10	121.00	25.70	50.20	72.60	110.80	217.00	11.00	136.20	80.90
1075	169 50	34.30	43.10	109.90	84.40	15.40	13.70	75.90	68,50	119.20	2.80	117.70	45.10
1076	176.20	38.60	79.40	118.90	116.00	40.20	10.50	83.10	78.10	160.30	20.30	105.60	55.00
7251	225.90	71.20	138.40	162.80	142.70	35,40	36.50	103.00	89.20	149.60	62.10	128.90	85.10
1078	250 31	02.86	218.70	207.90	123.70	41.60	85.40	109.50	111.70	206.60	56.40	122.50	99.10
1979	394.30	81.70	238.00	267.30	181.90	47.10	51.60	227.90	197.10	329.10	90.50	211.30	189.80
1980									;	0	6	00	700
1st quarter	489.80	105.10	204.00	280.00	139.20	60.60	48.60	325.30	202.90	378.90	33,30	251.90	202
2d quarter	373.00	47.20	185.40	153.60	133.20	23.10	26.80	584.50	226.90	179.00	الا. ⁷	222 50	142.50
3rd quarter	400.30	53.90	170.30	115.30	55.60	43.40	22.20	251.80	218.90	148.40	02.50	100.20	122 00
4th quarter	458.20	84.50	32.20	147.00	92.70	43.80	42.50	86.20	151.80	98.80	4.40	100.32	136.00
1980 average	432.20	70.80	190.80	167.00	102.80	44.60	34.20	306.50	208.00	301.00	43.60	241.80	167.90
•													
1981— 1st quarter	465.40	136.10	262.60	186.60	79.50	76.10	4.60	153.90	170.40	160.40	17.30	120.60	99.40
2d quarter													
30 quarter 4th quarter													
1981 average													

Source—Forest Service, U.S. Department of Agriculture. Pacific Korthwest Region includes Oregon and Washington.

 $^{^{}m l}$ Includes bid price plus deposits for sale-area betterment.

²Includes Port-Orford-cedar.

TOREST	MED I	3100	FVOI	JIDL								
	VOL UME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE
Western Oregon:												
Mount Hood	40,070	461.08	13,700	315.91	2,100	13.45	22,540	139.28	5,860	133.85	99,321	294.97
Rogue River	12,930	245.61	0	0	80	83.11	125	275.00	11,140	194.60	33,680	220.55 523.91
Siskiyou Siuslaw	53,458 164,660	584.80 444.38	0 0	0	0	0 0	960 16,986	18.12 187.79	140	9.15 0	63,662 192,240	403.16
Umpqua	77,420	445.54	Ö	0	700	128.60	5,700	60.07	4,510	27.56	116,535	313.80
Willamette	196,469	493.53	ŏ	ŏ	0	0	30,361	117.61	90	104.96	290,440	349.46
Total and average	545,007	472.55	13,700	315.91	2,880	43.38	76,672	134.26	21,740	142.00	795,878	358.91
Western Washington:												- 22
Gifford Pinchot	18,900 20,300	582.41	0	0	0	0 0	2,200	27.80 228.38	6,600 28,660	12.58	29,670	378.09 211.67
Mount Baker-Snoqualmie Olympic	25,135	358.33 270.79	0	0	0	0	24,601 41,345	242.38	2,000	158.68 65.56	91,856 77,915	221.42
o tymp to								242,30		03.30		221.42
Total and average	64,335	389.76	0	0	0	0	68,146	230.40	37,260	127.80	199,441	240.23
Total and average,												
western Oregon and western Washington	609,342	463.81	13,700	315.91	2,880	43.38	144,818	179.50	59,000	133.03	995,319	335.13
Eastern Oregon: Deschutes	0	0	3,310	6.70	26,047	332.30	٥	0	3,180	21 40	47 177	100.00
Fremont	ő	ŏ	3,310	0.70	18,400	296.02	ő	Õ	6,900	21.42 22.69	47,177 30,106	192.83 230.49
Malheur	ŏ	Ď	9,400	48.90	36,850	221.74	ŏ	ŏ	7,150	13.28	66,800	148.88
Ochoco	0	0	_ 0	0	. 0	0	0	0	0	0	0	0
Umatilla	0	0	7,400	171.95	16,200	179.07	0	0	4,500	17.20	30,000	142.99
Wallowa-Whitman Winema	0	0	10,000 4,250	53.87 889.34	7,035 52,500	23.34 345.01	0	0	5,300 17,450	207.69 95.56	54,520	34.06
			4,230			343.01			17,450	90,00	76,690	307.54
Total and average	0	0	34,360	176.74	157,032	276.70	0	0	44,480	71.16	305,293	182.49
Eastern Washington: Colville	0	0	8,055	124 62	0	0	0	0	1 200	14.00	10.075	105.05
Okanogan	0	0	18,421	124.62 14.62	7,529	104.91	0	0	1,200	14.93 0	12,275 25,950	106.05 40.82
Wenatchee	Ö	ŏ	10,795	19.50	5,161	282.95	ŏ	ŏ	4,852	6.31	22,594	76.07
Total and average	0	0	37,271	39.80	12,690	177.32	0	0	6,052	8.02	60,819	67.08
Total and average,												
eastern Oregon and												
eastern Washington	0	0	71,631	105.49	169,722	269.27	0	0	50,532	63.60	366,112	163.32
Total and average, Region 6	609,342	463.81	85,331	120 27	172 602	266 50	144 010	170 50	100 533	101.00	1 261 421	000 00
negron o	003,342	403.01	00,331	122.71	172,602	265.50	144,818	179.50	109,532	101.00	1,361,431	288.93
Total and average, Oregon	545,007	472.55	48,060	216.41	159,912	272.50	76,672	134.26	66,220	94.41	1,101,171	310.00
Total and average.												
Washington	64,335	389.76	37,271	39.80	12,690	117.32	68,146	230.40	43,312	111.06	260,260	199.77

Source—U.S. Department of Agriculture. Pacific Northwest Region includes Oregon and Washington.

lpreliminary.

Table 34--Volume of timber sold on publicly owned or managed lands, Montana and Idaho, 1976-81

(In thousand board feet, Scribner scale)

					1980	30			1981	
AGENCY	1976	1977	1978	1979	TOTAL	IST QTR.	1ST QTR.	20 QTR.	3D QTR.	4ТН ОТВ.
Montana: U.S. Forest Service <u>1</u> / U.S. Bur. Land Manage. <u>2</u> / U.S. Bur. Indian Affairs State of Montana	438,311 3,401 6,558 18,675	543,216 3,730 147,917 20,842	533,161 4,576 6,880 25,036	512,023 9,148 37,468 28,110	579,943 11,079 25,405 24,662	46,352 982 14,424 8,517	88,970 312 5,677 9,425			
Total	466,945	715,705	569,653	586,749	641,089	70,275	104,384			
Idaho: U.S. Forest Service <u>l/</u> U.S. Bur. Land Manage. <u>2/</u> U.S. Bur. Indian Affairs State of Idaho	622,131 2,475 3,473 97,178	783,631 16,090 13,534 124,325	836,629 27,656 8,491 120,261	843,992 778 1,609 179,307	828,507 19,283 2,381 222,137	117,129 4,694 0 52,397	171,166 464 0 1,170			
Total	725,257	937,580	993,039	1,025,686	1,072,308	174,220	172,800			
All public lands: U.S. Forest Service <u>l</u> / U.S. Bur. Land Manage. <u>2</u> / U.S. Bur. Indian Affairs State of Montana State of Idano	1,060,442 5,876 10,031 18,675 97,178	1,326,847 19,820 161,451 20,845 124,325	1,369,790 32,232 15,371 25,036	1,356,0151 9,926 39,077 28,110 179,307	1,408,405 30,362 27,786 24,662 222,137	163,481 5,676 14,424 8,517 52,397	260,136 776 5,677 9,425 1,170			
Total	1,192,202	1,653,285	1,562,690	1,612,435	1,713,397	244,495	277,184			

Source--respective agencies listed.

 1 Convertible products only.

2Does not include cull log sales.

Table 35--Average stumpage prices of timber sold on publicly owned or managed lands, Montana and Idaho, 1976-81

(In dollars per thousand board feet)

				ı	1980	20			1981		
AGENCY	1976	1977	1978	1979	AVERAGE	1ST QTR.	1ST QTR.	2D QTR.	3D QTR.	4ТН QTR.	AV
Montana: U.S. Forest Service <u>l</u> / U.S. Bur. Land Manage. <u>2</u> / U.S. Bur. Indian Affairs State of Montana	37.66 40.63 55.51 69.21	57.21 62.01 24.93 82.70	62.12 50.25 35.78 104.76	59.66 41.99 114.61 114.36	43.31 60.39 104.81 79.44	52.43 26.70 131.69 92.14	51.69. 33.19 59.13 98.94				
Average	39.19	51.31	63.58	65.52	47.43	75.16	56.31				
Idaho: U.S. Forest Service <u>l</u> / U.S. Bur. Land Manage. <u>2</u> / U.S. Bur. Indian Affairs State of Idaho	24.60 48.53 39.97 69.01	33.08 62.28 82.38 82.26	52.10 83.46 67.51 133.14	63.56 63.70 119.89 102.23	40.74 47.09 129.09 92.21	43.03 114.61 86.67	41.58 30.49 				
Average	30.71	40.81	62.92	70.41	51.71	58.08	41.69		:		
All public lands: U.S. Forest Service!/ U.S. Bur. Land Manage.!/ U.S. Bur. Indian Affairs State of Montana State of Idaho	30.00 43.96 50.13 69.21 69.01	42.96 62.23 29.75 82.70 82.26	56.00 78.75 53.31 104.76 133.14	62.09 43.69 114.83 114.36	41.80 51.94 106.53 79.44 92.21	45.70 99.41 131.69 92.14 86.67	45.04 31.58 59.13 98.94 62.41		: : :	i	İ
Average	34.03	45.35	63.16	68.63	50.11	62.37	47.20				

Source--respective agencies listed.

lprices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, quality, road costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stumpage prices include deposits for sale-area betterment.

2Does not include cull log sales.

Table 36--Average stumpage prices for sawtimber sold on National Forests by selected species, Northern Region, $1970-81^1$ (In dollars per thousand board feet)

LODGEPOLE ENGELMANN WESTERN PINE SPRUCE HEMLOCK CEDARS LARCH FIRS	4.10 9.00 1.70 10.20 10.40 4.80 8.30 13.30 2.90 9.10 17.30 4.90 16.50 27.00 12.90 28.50 34.30 19.20 38.30 65.80 42.60 45.20 66.30 46.10 19.40 39.10 28.90 26.50 38.90 29.20 19.20 10.90 2.00 42.50 20.30 4.80 16.70 42.20 9.60 45.80 52.90 9.30 38.30 61.40 11.90 72.00 72.20 20.20 44.70 85.80 42.50 144.90 69.60 37.30 42.70 44.10 171.80 123.20 73.80 30.10 53.80 123.30 58.90 103.50 32.50 87.30	
	19.10 28.00 11.20 23.00 35.50 65.90 66.50 65.90 63.50 117.80 22.40 36.20 56.80 91.40 96.60 122.70 113.50 146.00 127.20 185.60 112.70 80.10 51.10 92.70	
YEAR AND DOUGLAS— QUARTER FIR	1970 7.50 1971 10.10 1972 26.70 1973 50.70 1974 31.90 1975 14.40 1976 23.00 1977 41.50 1978 41.20 1979 51.90 1980 20.50 1981 20 1981 41.20 1981 41.20	

Source—Forest Service, U.S. Department of Agriculture. Northern Region includes Montana, northeastern Washington, northern Idahc Dakota, and northwestern South Dakota.

 $^{^{1}\}mathrm{Includes}$ bid price plus deposits for sale-area betterment.

Table 37--Volume of timber sold on publicly owned or managed lands in Alaska, 1976-81 (In thousand board feet, Scribner scale)

					I	1980		1981		
AGENCY	1976	1977	1978	1979	TOTAL	1ST OTR.	1ST 0TR. 1ST 0TR.	מדס וודג מדס מג מדח מל	TE O LIEV	Γ,
71						-		יאוף מכ	4 III QIK.	_
U.S. rorest Service1/	15,619	80	175,140	93,733	93,733 145,285	468	14 066			
U.S. Bur. Land Manage. 2/	215	54	142	22	125	2	000			
II C Bur Indian Aftering	,			I I	611	>	-			
o.o. bui. Illulall Arrairs	0	0	440	258,360	12,794	1,806	c			
State of Alaska	2,358	2,412	6,932	156,235	4 949	, [, ,			
					(† (*)	16067	3,34U	-		
Total	18,192	2,546	2,546 182,654	508,350 163,153	163,153	4,125 17,406	17,406			-

Source--respective agencies listed.

 $^{
m 1}$ Convertible products only.

2Does not include cull log sales or volume given away through free use permits.

Table 38—Average stumpage prices of timber sold on publicly owned or managed lands in Alaska, 1976-81

(In dollars per thousand board feet)

					16	1980			1981
AGENCY	1976	1977	1978	1979	AVERAGE	AVERAGE 1ST QTR.	1ST QTR.	20 QTR. 30 QTR.	3D QTR.
U.S. Forest Service <u>1</u> /	25.34	63.00	51.73	159.71	101.72	8.79	37.11		¦
U.S. Bur. Land Manage. $2/$	20.00	9.17	94.72	34.09	00.9	1	ł		
U.S. Bur. Indian Affairs	}	1	80.00	5.31	151.83	147.84	}		
State of Alaska	21.72	32.96	26.60	3.22	24.63	14.46	18.08		
Average	24.81	33.37	50.88	33.14	103.24	103.24 72.21	33.46		

Source--respective agencies listed. Includes products other than sawtimber.

Iprices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, ocosts, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stuniclude deposits for sale—area betterment and are for convertible products only.

 $^2\mathrm{Does}$ not include cull log sales or volume given away through free use permits.

YEAR AND QUARTER	SITKA SPRUCE	WESTERN HEMLOCK	CEDAR AND OTHER SPECIES	ALL SPECIES
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1st quarter 2d quarter 3d quarter 4th quarter	21.40 13.30 7.30 13.30 41.80 33.00 25.10 65.00 99.17 289.50 7.90 58.70 215.70	7.70 2.20 7.90 11.50 22.30 18.10 12.00 65.00 4.27 100.00 5.80 7.60 18.50 0	47.80 20.90 1.00 21.10 41.70 60.70 67.30 4.00 136.17 161.70 15.00 25.20 461.50 0	12.90 6.20 7.60 12.50 28.80 23.20 28.00 63.00 40.57 142.70 8.10 28.80 102.30 0
1980 average	213.30	18.40	437.40	101.10
1981 1st quarter 2d quarter 3d quarter 4th quarter	168.10	2.00	45.30	36.80
1981 average				

Source—Forest Service, U.S. Department of Agriculture. Alaska Region is the State of Alaska.

Table 40--Volume of timber sold on publicly owned or managed lands in California, 1976-81

(In thousand board feet, Scribner scale)

					190	1980			1981	
AGENCY	1976	1977	1978	1979	TOTAL	1ST QTR.	1ST QTR.	20 QTR.	30 QTR.	4ТН QТК.
U.S. Forest Service <u>l</u> /	1,443,372	1,716,954	,716,954 2,001,607 2,071,263	2,071,263	1,875,796	358,862R	280,004			
U.S. Bur. Land Manage. 2^{l}	18,769	15,326	13,107	4,195	17,203	2,444	1,872			
U.S. Bur. Indian Affairs	30,428	28,580	37,200	33,729	22,230	11,730	0			
State of California	39,150	13,317	27,333	21,833	30,328	13,382	0			ž.
Total	1,531,719	1,774,177	2,079,247	2,131,020	,774,177 2,079,247 2,131,020 1,945,557	386,418R	281,876			

Source--respective agencies listed.

1Convertible products only. Includes all of the Pacific Southwest Region and the portion of the Pacific Northwest Region in California. $^2\mathrm{Does}$ not include cull log sales or volume given away through free use permits.

R = revised.

note stumpage prices of timber sold on publicly owned or managed lands in California, 1976–81 (In dollars per thousand board feet)

					1980	0			1981	
AGENCY	1976	1077	9505							
		1107	1978	1979	Average	Average 1ST QTR.	1ST QTR.	1ST QTR. 20 OTR. 30 OTB	ath oth	ATO UTA
1.S. Forest Sourisell	,							r	• 427	יאות עוּא.
ייין פון אורבי	17.65	118.14	145.57	201,08	241 20	200				
U.S. Bir Land Manage 27	,				60.112	223.bbK	207.16			
cest sail - Land Manage. El	/1.35	150.92	96.39	102 59	172 95					
11.5 Bur Indian Acces	,				C7.6/1	134.44	169.86			
site and thought Arrange	111.02	132,22	125,34	157 70	150 00					
State of California	;			03.101	128.28	154.05	!			
orace of calliornia	142.04	137.13	273.35	370.76	283.94	339 12				
						14.	1			
Average	79.88	118.80	146.58	201.94	240 61					
				10.101	76.042	224.99R	206.92			

Source--respective agencies listed.

lprices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, quality, r costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stumpage pri include deposits for sale-area betterment.

2Does not include cull log sales or volume given away through free use permits.

R = revised.

25 mg

YEAR AND QUARTER	DOUGLAS- FIR	PONDEROSA AND JEFFREY PINES	SUGAR PINE	LODGEPOLE PINE	CEDARS	TRUE FIRS	ALL SPECIES
1970	25.60	32.20	38.60	3.70	14.00	4.20	32.00
1971	27.50	33.00	46.40	2.40	30.30	7.10	26.00
1972	40.70	65.80	66.60	5.40	50.10	30.20	47.40
1973	84.80	108.60	89.30	12.40	86.40	70.20	83.10
1974	87.00	101.40	104.00	6.50	112.00	41.70	81.80
1975	51.40	71.00	99.00	22.40	79.90	19.70	53.80
1976	76.00	101.80	185.00	6.50	84.00	23.40	80.40
1977	124.30	131.40	168.50	165.20	337.90	50.60	121.10
1978	131.10	164.70	169.20	136.20	516.40	7 9. 80	148.10
1979	186.60	239.00	375.40	25.40	497.10	96.00	206.20
1980							
1st quarter	209.50	199.70	476.80	541.80	784.50	87.40	227.50
2d quarter	101.80	173.50	511.20	274.10	648.90	56.90	195.20
3d quarter	181.70	231.70	804.90	20.20	518.20	185.10	288.40
4th quarter	360.40	140.20	452.20	59.90	120.00	55.80	201.00
1980 average	189.50	206.10	671.40	252.80	559.90	133.40	252.20
1981 1st quarter 2d quarter 3d quarter 4th quarter	194.70	354.20	388.60	117.20	58,70	95.30	204.70

Source--Forest Service, U.S. Department of Agriculture. Pacific Southwest Region is the State of California.

YEAR	ALLOWABLE CUT ²	UNCUT VOLUME UNDER CONTRACT	RATIO
1970 1971 1972 1973 1974 1975 1976 1977 1978 1979	1,151 1,196 1,249 1,196 1,196 1,196 1,183 1,183 1,183 1,183	2,041 1,876 1,665 1,390 1,503 1,838 2,077 2,066 2,204 2,224 2,484	1.8 1.6 1.3 1.2 1.3 1.5 1.7 1.7 1.9 2.0 2.2

Source--Bureau of Land Management.

 $^{^{1}\}mathrm{As}$ of December 31 of each year.

 $^{^2\}mbox{Includes}$ an estimated 24 million board feet for eastern Oregon.

QUARTER	SALES	VOLUME	SALES	VOL UME	SALES	VOLUME	SALES	VOL UME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME
	Number	Thousand bd ft	<u>Number</u>	Thousand bd ft										
1970	0		0		0		9	25,430	0		9	37,557	5	5,975
1971	0		0		0		8	20,285	0		21	64,198	ň	7,170
1972	0		0		0		23	84,440	Ō		0		ō	~-
1973	0		0		2	25,600	12	18,740	0		0		Ō	
1974	4	30,100	0		4	46,300	33	172,615	1	650	8	26,860	11	63,527
1975	4	13,855	0		5	66,920	18	147,050	2	2,135	8	56,320	17	66,390
1976	1	2,263	0		1	15,200	7	68,250	Ö	´	2	8,350	4	10,658
1977	3	13,800	7	63,290	8	69,000	13	192,500	0		10	70,450	15	76,379
1978	4	43,500	0	·	1	357	15	161,500	0		0		20	83,836
1979	5	42,760	4	2,150	11	79,460	0		Ō		19	11,575	34	86,586
1980 1981	2	20,400	3	2,032	6	44,360	16	113,140	0		18	6,763	44	26,525
1st qtr. 2d qtr. 3d qtr. 4th qtr.	1	165	0		0		Q		0		3	416	7	30,640

1981 total

	100	1000	OK	ANOGAN	OLY	MPIC	ROGUE	RIVER	SIS	KIYOU	SIU	SLAW	UMA	ΓΙLLA
YEAR AND QUARTER	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME
	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft						
1970	0		3	18,700	7	26,675	0		0		0		2	22,000
1971	0	****	4	14,860	3	15,140	0		0		0		0	
1972	0		0		8	32,897	0		0		. 8	26,356	11	198,116
1973	0		0		22	92,199	0	~~	17	94,680	14	72,701	5	22,400
1974	O		3	19,000	12	78,990	28	98,752	12	52,775	34	174,471	11	74,710
1975	3	39,550	2	21,000	8	53,842	24	143,665	22	59,331	26	201,478	5	28,620
1976	3	19,270	2	9,300	5	45,579	18	46,254	. 7	22,335	17	118,763	6	23,110
1977	0		1	11,500	2	30,926	25	100,807	14	58,980	17	91,027	7	31,100
1978	5	34,300	0		6	44,615	47	171,251	13	62,300	39	231,303	Q.	
1979	3	23,500	7	20,105	12	106,105	50	118,818	2	270	16	120,834	4	35,500
1980	1	7,700	2	10,600	12	69,100	31	123,125	7	29,510	7	45,137	3	18,200
1981									_					
1st qtr. 2d qtr. 3d qtr. 4th qtr.	0		0		0		16	31,020	0	***	20	98,274	1	6,500

1981 total

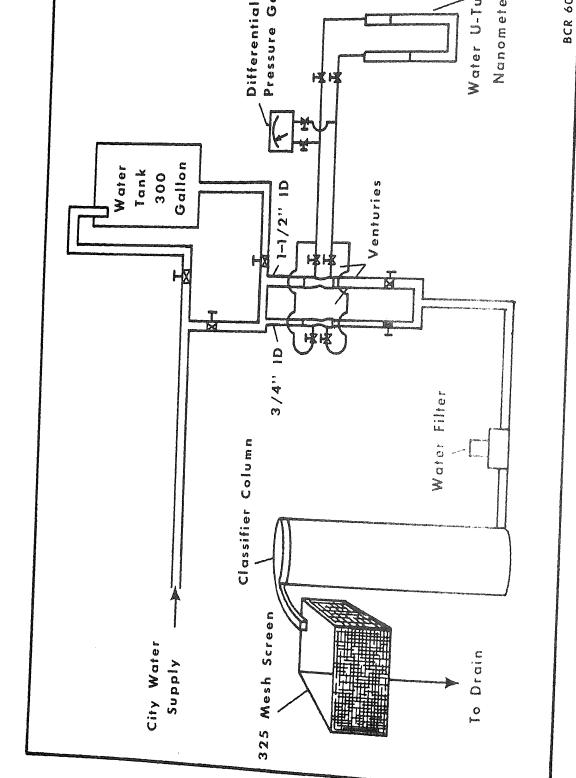
	Uł	4PQUA	WALLOWA-	-WHITMAN	WENA	TCHEE	WILL	AMETTE	WI	NEMA	ALL	FORESTS
YEAR AND QUARTER	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME
	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft
1970	2	7,316	0		3	3,386	0		0	~-	40	147,039
1971	0		0		0		0		0		37	121,653
1972	0		0		0		0		0		50	341,809
1973	0		8	77,400	o.	-~	7	58,510	5	22,460	92	484,690
1974	22	124,807	0		0		. 7	61,520	5	35,550	195	1,060,627
1975	29	146,668	0		2	17,400	10	137,810	9	69,600	194	1,271,634
1976	21	55,093	0		Ō		19	121,100	5	38,040	118	603,565
1977	29	128,705	0		0		48	174,585	.8	35,110	207	1,148,159
1978	29	125,330	0		0		33	177,660	13	60,006	225	1,195,958
1979	35	169,212	0		5	23,100	53	146,366	6 4	59,050	266 281	1,045,391
1980	31	166,650	7	1,799	4	18,000	83	197,229	4	30,400	501	930,670
1981				100	,	500		2 026	5	50,450	91	311,521
1st qtr. 2d qtr. 3d qtr. 4th qtr.	30	91,385	1	135	1	500	6	2,036	ט	au,4aU	21	311,521

1981 total

Source--Forest Service, U.S. Department of Agriculture. Pacific Northwest Region includes Oregon and Washington.

 $¹_{
m July}$ 1, 1974, Colville National Forest in Washington became part of the Pacific Northwest Region.

 $^{^2\}mathrm{July}$ 1, 1974, Snoqualmie National Forest was merged with the Mount Baker National Forest.



selenium, vanadium, zinc, antimony, sodium, and potassium. The cadmium lead concentrations were too low in each of these coals to be detected this flame technique; therefore, these elements were then determined by flameless graphite furnace technique utilizing apparatus specifically p chased for this determination. The apparatus will also be useful for o

low-concentration level determinations.

The solutions for flame and furnace atomic absorption as well as f atomic emission were prepared by dissolving the ash in teflon beakers w aqua regia/hydrofluoric acid (1:1) by boiling to dryness, adding nitric and diluting to volume.

developed at BCR based on Eschka fusion, hydride generation, and atomic absorption using a hydrogen-argon flame. This procedure is presently b considered for round-robin testing by ASTM Committee DO5 on Coal and Co

Mercury was determined by a combustion bomb method developed at BC

by a double-gold amalgamation system constructed at BCR. Both techniqu involve flameless atomic absorption and both are being considered for ro

Arsenic, selenium, and antimony were determined by a unique proced

robin testing by ASTM Committee DO5 on Coal and Coke. The first method been tested with a great deal of success. Testing of the double-gold a gamation system has been hampered by so few of the systems being availa Fluorine was determined by a combustion bomb-selective ion electro method. As the work progresses, the analytical techniques used, partic for the trace-element determinations, including the most recent refinem are being written, tested, and modified where needed. Later they will incorporated into an analytical procedures manual for submission with t final report for this sponsored program.

The results of analyses are displayed on data sheets developed to the results of each analytical determination for each of the various frobtained during the cleaning. One example of these is shown as Figure which contains the ash content for all of the fractions obtained during cleaning of coal 1R, the first coal. From the data in this figure and the other similar data sheets, obvious analytical errors can be immediated. In this case, they could be observed readily as interruptions the trend of low to high ash content from clean coal to refuse fraction

With the voluminous data being obtained during the course of this proje would be easy to miss such simple errors caused, perhaps, by an incorre recorded sample number. In one case in a previous study, each fraction tained had a higher concentration value than the feed from which it cam This was traced to a dilution error during analysis. Displaying the dain Figure 6 minimizes the chances for these kinds of errors.

The analytical results for the individual samples are displayed as Figure 7. The individual samples were also divided into groups for a c

1-1/4" x 30M 26.8 15.8 6.22 5.86 19.2 22.8 41.6 55.8 79.4 78.6	percent		ROM 19.1		Coal:	1.8	
×			split			İ	
. 2 2 2 2 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	Screened 30 x 270M	-270M		-30M	sp	split -100M	MO
. 5	.8 13.0	21.1		22.3		2	21.9
9. 4.	36 6.57 8.8.47		-270M	200 × 270M	140 x 200M	100 × 140M	+100
			21.8	18.2	19.8		27
				6.14	5.38	4.46	7
				17.2	16.2	12.8	
				51.2	52.8	49.0	
				60.2	65.2	8.69	
200 -270M × 270M	140 M x 200M	100 × 140M	70 × 100M	50 × 70M	40 × 50M	30 × 40M	
31.4 21.2	2 19.9	17.2	16.9	- 15		- 8	
-				· —	7./1	8.77	
4.73	3 4.76	4.16	3.57	3,22	3,28	4.22	
7	The second secon	**************************************	9.64	8.75	8.68	12.5	
£		-0. -0.} -1.	90. 7.}	39.0	45.5	58.2	

PROXIMA	TE, %		ELEMENT, ppm	
Moistur	e .	0.64	Arsenic	15.8
Ash		8.47	Beryllium	1.34
Volatil	e Matter	32.8	Cadmium	0.045
Fixed C	arbon	58.7	Chromium	16.3
ULTIMAT	E, %		Copper	13.7
Carbon	_	78.4	Fluorine	65.9
Hydroge	n _	5.20	Lead	6.64
Nitroge	n _	1.44	Manganese	21.1
Sulfur	_	1.48	Mercury (ppb)	384
Chlorin	e _	0.20	Nickel	14.1
0xygen		4.81	Selenium	3.08
SULFUR	FORMS, %		Vanadium	30.4
Sulfate	-	0.00	Zinc	19.9
Pyritic	_	0.91	Antimony	0.94
Organic		0.57		
MISCELL	ANEOUS			
Calorif Btu/	ic Value lb	13,934		
MAJORS	IN ASH, %			
SiO ₂	45.4		Silicon	18,200
Al ₂ 0 ₃	25.7		Aluminum	11,700
Fe ₂ O ₃	16.0		Iron	9,620
MgO	0.86		Magnesium	450
CaO	5.82		Calcium	3,580
T102	1.38		Titanium	711
Mn0			Manganese	
Na ₂ O			Sodium	135
к20			Potassium	1,490
so ₃	1.52			
P2 05	0.56		Phosphorus	210

development in sufficient detail for use by coal industry and other tories involved in similar work.

Petrographic Methods Petrographic analyses were employed to supplement the chemic

designed to characterize coal separates evolved from the gravity and sizing techniques. These analyses involve the use of a light to identify and measure coal constituents and included impurities up each separate. The following analyses were used to optically each sample:

Coal composition: To identify and quantify the organic cons ents characterizing the subject separate.

Pyrite mode of occurence: To determine the relative associa

of the pyrite impurity with the coal. (Free, surface, or encased Pyrite size: To measure and quantify the mean projected are eter of the pyrite associated with the coal. Results of the petrographic analyses will not be discussed to

Data Evaluation

brief paper.

Further evaluation of the data was aided by use of a compute

balances were calculated and concentrations of the products were (a) based on the ultra-clean and clean coal fractions No. 1 and on the ultra-clean and clean coal as well as the non-pyrite refu

No. 1, 2, and 3; and (c) based on the middlings fractions No. 2 might, in a real situation, be subjected to additional cleaning.

of the computer printout for the program written for the mass ba culations is presented in Table 1. A differential value between and composite is also calculated and displayed in order that jud be made on the entire operation including the cleaning and analy

Most of these calculated values might not be needed to eval to reenter all of the data at some later time. For one coal, th

coal and each group; however, they will be available and are eas while the data are first being entered into the computer rather balances for 37 constituents and 18 different groups of feeds an

fractions could result in a total of almost 700 sets of individu tions, such as that displayed in Table 1, available for evaluati

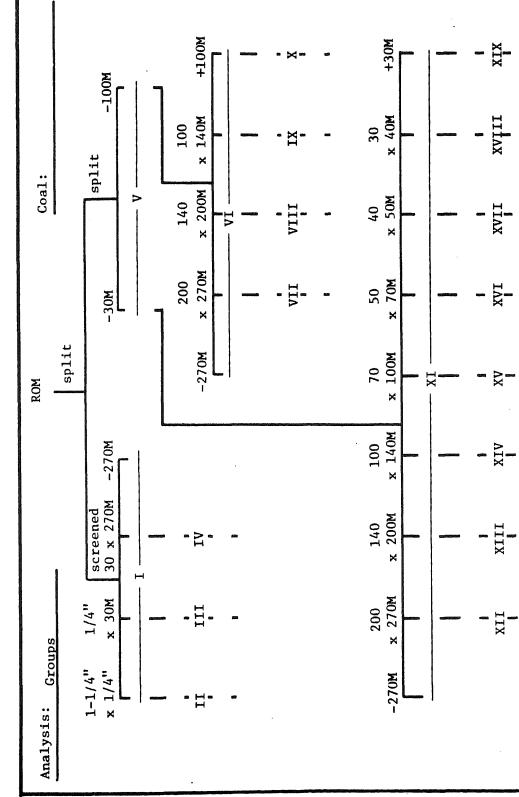


TABLE 1. SAMPLE PRINTOUT FROM MASS BALANCE CALCULATION PROGRAM

	DALIANOL OF	MODERITOR I ROCKER	
FRACTION NUMBER	WEIGHT FRACTION	SULFUR CONCENTRATION	
1	0.574	1.09	=

2	0.155
3	0.055
,	

WEIGHTED CONCENTRATI

0.626

0.273

			3.30	0.773
		1.000		1.881
[C]	IN FEED	= 1.76	(COMPFEED)	DIFFERENTIAL

IN	FEED	= 1.76	(COMPFEED)	DIFFERE
IN	CLEANED COAL	= 1.232		% REMO

	(00111	·	DIF.	FERENITAL
2			%	REMOVED
}			.L. av	Table 10

[C]	IN	CLEANED COAL	=	1 222			
• •		COAL	_	1.232	%	REMOVED	100
*[C]	IN	CLEANED COAL	=	1.413	*%	REMOVED	1002
[C]	IN	MIDDLINGS	=	2.294	*%	YIELD	
[C]	IN	REFUSE	=	3.625		YIELD	
					/0	LIELD	200

uent with the percent removed of every other constituent. This was dor an additional means of comparing the effectiveness of the fugitive elem removal of the two coals. At this time, the percent removed was select as the parameter to be evaluated. Later, when data for more coals are able, relationships between concentrations will be examined more thorough

RESULTS AND DISCUSSION

Cleaning, analyses, and data evaluation of two coals are complete. coal is a mixture of Upper and Lower Freeport seams and the other an II No. 6 seam. Work on additional coals is in progress. The data were us evaluating the effect of such cleaning on fugitive elements.

Coal Sampling

A list of the twenty coal seams to be sampled is shown in Table 2. of these have already been acquired and are available to the project.

Coal Cleaning

The first three coals were extensively cleaned using both Procedur and Procedure B; the fourth coal involved only the shorter Procedure A. the weight percent, ash, total sulfur, and calorific value data for the two coals, the cleaning strategies employed were particularly effective the separations needed to attain the objectives of the project were being achieved.

Washability studies were utilized primarily to determine how much could be produced at a given specific gravity and to define the ash and fur characteristics of the coal at that gravity. A washability study we made by testing coal samples at carefully controlled specific gravities analyzing the specific gravity fractions for ash and sulfur contents. table was developed detailing the weight percentages and the ash and su analysis for each fraction. The data were then mathematically combined "cumulative float" and "cumulative sink" for both ash and sulfur and we utilized to develop "washability curves" which helped to characterize to

coal. One example of the washability tables developed for this study, one for the first coal, is presented in Table 3. The tables detail the aration gravities, the corresponding weight percentages, and the ash as sulfur analyses for each of the three size fractions.

The washability curves for the 31.8 x 6.35-mm (1-1/4 x 1/4-inch)

The washability curves for the 31.8 x 6.35-mm $(1-1/4 \times 1/4-inch)$ fin of coal 1R which was cleaned utilizing the heavy media unit are stin Figure 9. Five curves are plotted on the chart: cumulative float a (CFA), cumulative float sulfur (CFS), cumulative sink ash (CSA), cumulative sink sulfur (CSS), and the yield curve. As stated previously, these curves are plotted on the stated previously, these curves are plotted on the chart:

sink sulfur (CSS), and the yield curve. As stated previously, these contains to determine how much coal may be produced at a given special

TABLE 2. COALS TO BE USED IN BCR FUGITIVE ELEMENT STUDY

Sample	Seam	Sample	Seam
1	Upper/Lower Freeport	11	Pocahontas No. 3
2	Illinois No. 6	12	Stockton
3	Rosebud	13	Sewell
4	Beulah-Zap	14	Mary Lee
5	Hannah No. 60	15	Kentucky No. 9
6	Adaville No. 1	16	Illinois No. 5
7.	Castle Gate B	17	Imboden
8	Lower Kit- taning	18	Upper Elk- horn
9	Pittsburgh	19	Pittsburgh
10	Meigs Creek	20	Lower Kit- taning

WASHABILITY ANALYSIS OF COAL 1R	
TABLE 3.	

~	
COAL 1R	
0F (
ANALYSIS	
WASHABILITY ANALYSIS	
TABLE 3.	

Cumulative Rejects, per

Cumulative Recovery, percent

 $1-1/4 \times 1/4$ Inch Heavy Media - coarse

Group II

Sulfu

Ash

Yield

Sulfur

Ash

Yield

Sulfur

Ash

Yield

Float

Sink

percent

Separates,

Specific Gravity

3.50

26.0 52.6 71.7 79.4

100.0 42.6 27.1 21.6

1.23 1.41

9.0 11.3 26.0

72.9 78.4 57.4

6.2 19.2 41.6 79.4

57.4 15.5 5.5 21.6

1.35 1.55 1.80

1.55

1.80

1.35

100.0

1.09

6.2

1.091.76 3.80 3.58

1.90

2.2 6.8 6.8 8.9

15.7 54.2 69.9 78.6

100.0 20.4 13.6 8.4

1.06 1.19 1.44 2.24

5.9 7.2 10.0 15.7

79.6 86.4 91.6 100.0

2.64 5.67

5.9 22.8 55.8 78.6

11.0

8.4

1.35 1.55 1.80

1.06

9.64 6.8 5.2

1.35 1.55 30 x 270 Mesh Hydraulic Classifier

Group IV

1/4 Inch x 30 Mesh Heavy Media - fine

Group III

2.2 2.8 2.8 6.0

12.9 15.9 33.0 69.2

1.06 1.31 1.56 2.29

6.6 7.7 9.6 12.9

31.9 79.5 94.4 100.0

1.06 1.48 2.90 14.5

8.5 19.4 69.2

31.9 47.6 14.9 5.6

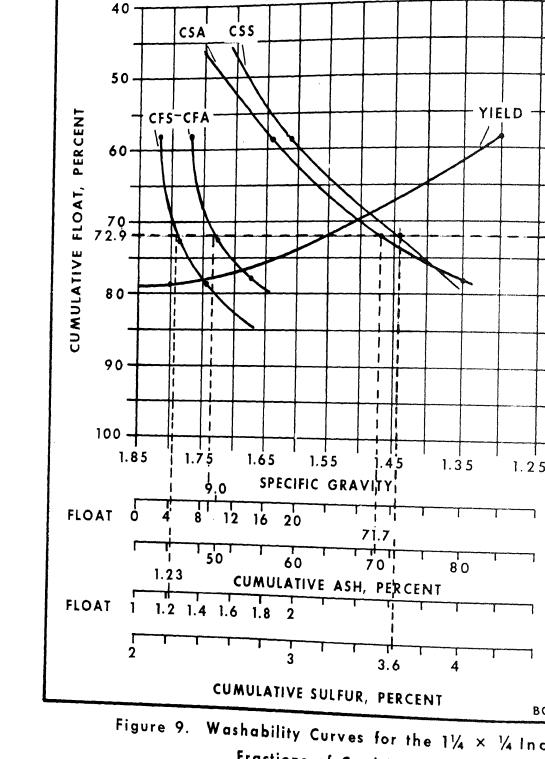
1.42 2.46 1.31 1.27

9.9

Average

20.5 68.1

100.0



Fractions of Coal 1R

ity were chosen for the cleaning gravity of the 31.8×6.35 -mm (1-1/4 x 1 inch) fraction of coal 1R, the following results would be expected: the yield in the float fraction would be 72.9 percent of the total feed coal, the float fraction would contain 9 percent ash and 1.23 percent sulfur, t sink fraction would contain 71.7 percent ash and 3.6 percent sulfur. It should also be noted that the slope of the cumulative float curves gives quick estimate of the difficulty of cleaning a coal. The greater the slot the more near-gravity material and the more difficult the coal is to clean

By referring to Figure 9, it can be seen that if a 1.55 specific gra

By interpreting the data presented and by utilizing the washability curves, general statements can be made about the characteristics of the t coals and the response of the coals to cleaning.

For example, it can be inferred that coal 2R is more resistant to put

verization than 1R. Coal 2R contains a higher percentage of material in coarse size fraction, 31.8 x 6.35-mm (1-1/4 x 1/4-inch), and a lower percentage in the fines, 30 x 270-mesh, than coal 1R. The higher percentage the coarse screen fraction of coal 2R indicates that less degradation occurred during the screening, implying that coal 2R is harder than 1R.

When compared at a 1.45 specific gravity, the 6.35-mm $(1/4-inch) \times 3$ mesh fraction showed the best ash reduction potential for both coals. The 31.8 x 6.35-mm $(1-1/4 \times 1/4-inch)$ fraction of coal 1R had the highest per centage ash reduction (72 percent), but the feed ash was much higher than in the 6.35-mm $(1/4-inch) \times 30$ -mesh fraction, which yielded a higher flow ash even with the 72 percent reduction. The ash reduction potential at the

1.45 gravity was poor for both coals at the 30×270 -mesh size range. Fr the washability curves, a lower specific gravity separation for the 30×270 -mesh size range.

Coal 1R showed better total sulfur reduction potentials than 2R for size ranges at the 1.45 specific gravity. Coal 1R inherently has a lower sulfur content at the run-of-mine level and also proved, even for the 30 x 270-mesh fraction, to be easier to clean to an acceptable sulfur level.

270-mesh fractions would yield a better cleaning response.

The changes in the Btu levels between the raw coals and the coals was at 1.45 gravity were not significant. Only the 31.8×6.35 -mm (1-1/4 x 1 inch) fraction of coal 1R showed a reasonable increase, 22.9 percent. The fine fractions, 30×270 -mesh, of both coals showed a large reduction in Btu's when cleaned at 1.45 gravity. Again, a specific gravity lower than 1.45 would show a better response for the fines of both coals.

project such as the magnetite used in the heavy media separation Every determination was done in duplicate. Lack of duplicate immediately precipitated an additional determination. Whenever as time allowed, more than one procedure was used for the trace terminations as a check on the accuracy of the analytical value Finally, as a continual check on the analytical procedures project, National Bureau of Standards (NBS) certified reference SRM-1632 Coal and SRM-1633 Fly Ash, were analyzed along with ea

for the same 14 elements is only 8 ppm.

the trace elements for coal 1R is 27 ppm; for coal 2R, it is 2 coal 3R, it is 15 ppm. For the lignite, coal 4R, the average c

coals, including the run-of-mine sample, were determined.

samples was a continuing problem throughout the study. Instan chromium, copper, lead, nickel, and zinc contamination were iddocumented. These will be described thoroughly both in a fort and in a report on analytical procedures. Contamination was he mum by routinely analyzing reagent blanks and other material us

of-mine coal and its cleaned fractions. One example of the type ment normally obtained between the determined values and the MI

for the various individual cleaning schemes for each coal.

for each of the determined constituents were calculated: (a) t integrity of the cleaned fractions and the validity of the anal by comparing the summation of the materials in each fraction wi material, and (b) to evaluate the reduction or enrichment of ea

A more thorough description of the analytical procedures as precision and accuracy studies is programmed at the end of the funded portion of this program, when the twenty coals have been

Thirty-eight constituents of samples of each of the first

Con

The

analyzed and the effect of the cleaning on fugitive elements has mined.

values is presented in Table 5.

Mass Balance Calculations

The analytical data for each coal were used in calculating

ent as a result of the cleaning process. For each constituent, the concentration determined in a par rated fraction was multiplied by the weight fraction of the fee reported to that zone. The weighted concentrations thus obtain

TABLE 4. COMPARISON OF CONCENTRATIONS OF RUN-OF-MINE COALS 1R, 2R, 3R, AND 4R (dry coal basis)

	Coal 1R	Coal 2R	Coal 3R	Coal
Ash, percent	22.3	16.0	15.8	11.
Total Sulfur, percent	2.30	2.73	1.18	0.8
Chlorine, percent	0.12	0.33	0.01	0.0
Pyritic Sulfur, percent	1.78	2.01	1.02	0.7
Organic Sulfur, percent	0.46	0.50	0.14	0.1
Arsenic, ppm	40.2	11.0	8.54	10.
Beryllium, ppm	1.84	1.10	0.87	0.7
Cadmium, ppm	0.08	0.47	0.12	0.0
Chromium, ppm	29.7	21.1	8.21	5.1
Copper, ppm	22.1	11.0	13.2	6.9
Fluorine, ppm	115	113	63.6	32.
Lead, ppm	15.4	21.8	12.8	1.8
Manganese, ppm	50.0	36.8	65.2	33.
Mercury, ppb	662	154	154	11
Nickel, ppm	20.9	18.4	4.98	4.6
Selenium, ppm	6.20	1.83	1.61	0.9
Vanadium, ppm	44.4	26.2	14.0	10.
Zinc, ppm	35.5	91.8	12.8	3.4
Antimony, ppm	1.09	0.40	1.78	0.5
Sodium, ppm	448	1,230	248	6,63
Potassium, ppm	5,460	2,980	1,110	57
Silicon, ppm	57,800	37,900	39,800	14,50
Aluminum, ppm	30,800	17,700	20,200	6,47
Iron, ppm	21,100	19,100	8,560	7,84
Magnesium, ppm	1,360	870	3,150	4,06
Calcium, ppm	2,090	3,110	6,790	16,10
Titanium, ppm	1,670	1,010	1,090	37
Phosphorus, ppm	260	160	85	14

Calorific Value, Btu/lb 11,640 11,902 10,990

10,55

TABLE 5. COMPARISON OF TRACE ELEMENT CONCENTRATIONS IN SRM-1632 COAL WITH NBS CERTIFIED VALUES (All values in ppm on a dry coal basis)

Element	Average ppm <u>Determined</u>	NBS Value,
Antimony Arsenic Beryllium Cadmium Chromium Copper Lead Manganese Nickel Potassium Selenium Sodium Vanadium Zinc	3.47* 6.22 1.63 0.17 20.5 17.7 31.7 45.6 14.1 2,680* 2.88 362* 36.4 41.6	not certified 5.9 ± 0.6 1.5 [†] 0.19 ± 0.03 20.2 ± 0.5 18 ± 2 30 ± 9 40 ± 3 15 ± 1 not certified 2.9 ± 0.3 not certified 35 ± 3 37 ± 4

* In agreement with other published values.

[†] Informational value.

I INIOIMALIONAL VALUE

the componentation and the reca.

likely) the refuse.

coal 4R.

The differential between composite and feed was obtained from each π balance calculation as follows:

Differential = $\frac{\text{Composite Value - Feed Value}}{\text{Feed Value}} \times 100$

These values, since they indicate the extent of agreement between feed an product constituents, can offer much insight into both the cleaning and the analytical study. Judgments are possible on the cleaning process based of the agreement of many of the constituents within any one cleaning operation Poor agreement generally might indicate problems with the integrity of the samples obtained by cleaning; good agreement with the exception of one or two constituents, might indicate problems in the analytical determination of the constituents. A consistent positive or negative bias would indicate gain or loss of a constituent during cleaning or analysis, or analytical

problems with certain of the fractions, perhaps the clean coal or (more

The average percent differentials for each of the first four coals a summarized in Table 6. The values presented in the table are the average (absolute value) from as many as 18 values from the individual cleaning of erations. Low values indicate good agreement between composite and feed. Obviously, there is a great deal of satisfaction with these values. For most part, the agreement was better for coals 1R, 2R, and 3R than it was

Some of the lack of agreement can be attributed to the low concentrations of trace constituents associated with this fourth coal. The concentrations in solution were often at or near the detection limits of the analytical methods. Additionally, slight contamination of trace constitution of trace and tolerated in previous analyses exerted a greater influence on results at the low concentration levels. Such low concentrations will probably be experienced with other coals for this project.

Effect of Cleaning on Distribution and Removal

The analytical data were used in evaluating the effect of cleaning trun-of-mine coals on fugitive element removal. An example of the type of data available, a summary of the percent of each constituent removed as a result of cleaning coal IR, is presented in Table 7.

This calculation assumes the first two fractions as the cleaned coal the last two as the refuse. The corresponding product recovery for each group is presented at the top of each column in this table. Most of the stituents which were concentrated, not removed, by the cleaning were not cluded in this table. For the most part, these were inherent parts of the

COALS 1R, 2R, 3R, and 4R

	Coal 1R	Coal 2R	Coal 3R
4.4	2	3	5
Ash Volatile Matter	2	1	1
	1	1	1
Fixed Carbon	-	_	
Carbon	1	1	1
Hydrogen	2	3	3 5 5
Nitrogen	2	2	5
Total Sulfur	4	2	5
		•	7.0
Chlorine	11	6	19
Pyritic Sulfur	5	3	7
Organic Sulfur	5	3	11
Calorific Value	1	1	1
Arsenic	15	8	11
Beryllium	4	3	5
Cadmium	14	21	9
Chromiun	3	8	7
Copper	14	17	8
Fluorine	9	7	6
Lead	14	14	9
Manganese	3	7	4
Mercury	13	61	18
Nickel	9	8	25
0-1			-
Selenium	6	15	7
Vanadium	5	5	3
Zinc	6	21	23
Antimony	8	12	11
Sodium	10	1.1	7.0
Potassium	8	11	10
Silicon	٠ /	4	4
Aluminum	7	4	4
Iron	4 5	4	3 9
	J	5	9
Magnesium	7	4	7.3
Calcium	7	7	11
Titanium	3	4	12
Phosphorus	6		5
	•	11	4
Average	6	9	8

Constituent								G	ROUP	•						
H.	<u> 11</u>	III	IV	XII	XIII	XIV	\underline{xv}	XVI	XVII	XVIII	XIX	VII	VIII	IX	X	Av.
suc	70	0.6	90	71	i.c				overy,	percer	_	00	•	-	٠.	
	<u>73</u>	<u>86</u>	<u>80</u>	<u>71</u>	76	<u>79</u>	<u>80</u>	83	<u>81</u>	<u>76</u>	<u>69</u>	82	<u>82</u>	<u>75</u>	<u>63</u>	<u>77</u>
Ash	75	60	52	73	69	67	70	6 6	70	73	71	52	55	71	81	67
s _T	52	54	54	78	71	65	66	60	62	66	76	68	63	72	82	66
C1	8	4	15	14	11	11	7	5	6	8	8	8	7	10	13	9
Spyr	65	69	6 6	89	83	79	82	78	80	81	8 6	80	78	85	91	79
Sorg	10	6	15	18	14	13	12	7	8	8	10	11	10	13	26	12
As	82	79	71	92	88	88	91	8 6	89	88	9 3	87	86	93	97	87
Вe	45	22	26	38	37	28	29	26	29	38	4 4	23	25	37	50	33
Cd	63	53	52	64	68	63	66	63	78	67	69	58	56	66	78	64
Cr	64	41	34	51	48	45	50	46	51	56	60	35	39	55	65	49
Cu	61	50	48	6 6	63	57	61	55	58	64	64	49	48	64	76	59
F	61	42	42	55	56	53	56	43	51	55	61	30	31	49	67	50
Pb	71	62	59	71	70	72	73	73	75	81	65	60	6 6	82	88	71
Mn	89	7 7	58	85	83	82	85	81	85	87	82	69	75	87	93	81
Hg	55	67	69	73	72	71	65	71	70	76	82	6 8	64	59	92	70
Ni	53	42	42	6 0	58	64	55	45	5 0	61	64	46	49	60	72	5 5
Se	44	65	67	82	78	73	75	74	72	79	83	74	72	80	88	74
v	63	36	31	47	39	41	42	39	44	55	58	30	32	52	66	45
Zn	74	58	45	71	6 6	61	66	62	6 5	71	65	51	51	6 7	78	63
Sb	29	33	28	36	42	30	35	22	3 2	28	52	28	29	41	60	35
Na	73	46	45	66	61	56	61	56	61	65	64	42	46	62	73	58
K	80	67	5 5	73	69	53	72	69	74	78	72	49	54	73	83	6 8
Si	77	61	51	72	68	67	69	68	71	74	71	49	54	71	80	67
Al	69	52	46	65	6 0	59	61	58	62	6 8	64	42	47	63	73	59
Fe	73	72	67	91	85	84	86	83	84	87	87	82	78	9 0	94	83
Mg	85	67	52	72	69	70	73	72	77	84	75	48	55	74	84	70
Ca	53	42	38	77	76	69	67	58	5 8	59	62	59	59	68	76	61
Ti	68	. 49	42	59	56	52	55	52	58	64	62	43	42	6 0	71	56
P	46	24	34	51	44	38	43	37	31	43	53	33	35	45	61	41
Aver- age	60	50	47	63	61	58	6 0	56	59	63	64	49	50	62	74	58
± C1			17		_ 1	ر د										

amounts in the feed.

are cleaned.

The averages by group and by constituent reflect generally go of most of the constituents. Arsenic, iron, manganese, pyritic su nium, lead, mercury, and magnesium were removed most effectively. antimony, phosphorus, and vanadium were removed least effectively. and organic sulfur were actually concentrated slightly in the clear

Similar data are available for each coal, assuming either the or first three fractions from the heavy media or the hydraulic cla separations as the cleaned coal. The data are further summarized, i by constituent for the first four coals. The values presented in are the averages from the individual values for each of the cleani tions, for example, from the last column on the right in Table 7.

The differences in the effectiveness of cleaning each coal car be seen from the data in Table 8. Most constituents were removed fectively from coal IR than from the other coals, but the product was also the lowest for this coal. Cleaning was least effective w

4R, the lignite. However, the principal reason for this is simply concentrations of the impurities in this coal, as previously displa Table 4, were relatively low prior to cleaning. It must be pointed out at the same time that the calorific va coal was also the lowest of the four. Perhaps the concept of a ca expression relating the concentration of impurities per calorific

ilar to the "pounds of sulfur per million Btu's," is needed to comtrace impurities in a wide variety of coals on an equal basis.

Differences in the relative rates of removal for each coal can observed from the data in Table 8. Cadmium and zinc were removed a tively from coal 2R than from the others. They were also present concentrations in this coal from the Illinois basin than in the otl

Linear correlation coefficients and F-test ratios were calcula the constituents to demonstrate the relationships between the perce of each constituent with the percent removed of every other constit relationships were evaluated among "percent" of the constituents re group rather than among "concentration" of each constituent removed This was done simply because two coals are not a statistically sign representation to permit drawing any specific conclusions concerning general and the effect of cleaning them on fugitive element removal

tration data will prove more meaningful later in the study when more

FOR ALL GROUPS

	Coal 1R	Coal 2R	Coal 3R	Coa
Product Recovery	77	87	87	
Btu Recovery	91	97	92	
Ash	67	48	41	
Total Sulfur	66	46	56	
Chlorine	9	8	16	
Pyritic Sulfur	79	55	61	
Organic Sulfur	12	9	16	
Arsenic	87	53	70	
Beryllium	33	20	21	
Cadmium	64	77	34	
Chromium	49	28	29	
Copper	59	37	28	
Fluorine	50	33	26	
Lead	71	61	31	
Manganese	81	65	20	
Mercury	70	42	41	
Nickel	55	25	27	
Selenium	74	34	45	
Vanadium	45	23	25	
Zinc	63	71	30	
Antimony	35	19	22	
Sodium	58	25	28	
Potassium	68	39	53	
Silicon	67	43	43	
Aluminum	59	42	37	
Iron	83	65	76	
Magnesium	70	42	13	
Calcium	61	72	14	
Titanium	56	34	33	
Phosphorus	41	66	21	
Average	58	42	34	
The F-statistic	was then utilize	ed in evaluat	ing the rela	itions
at the selected confi	dence level. T	he relationsh	nips are summ	narize
Table 9 for the first	two coals. On	ly those havi	ing the highe	est de
of correlation are li	sted. Even wit	h the imperfe	ect means of	evalu

These studies with the first new coars, as well as previous cleaning studies at BCR with eight coals have confirmed that remo potentially harm ul trace elements can be effected by coal clean i studies thus far with the coals reported here revealed differing to the various cleaning processes. Generalizations concerning the cleaning on fugitive elements are not possible at this time. sions concerning elemental distributions are not possible either Some trends have already been noted and these will be reexamined

> Studies with additional coals are planned and already under way. The program is flexibly designed to add or delete constituen by mutual agreement between the sponsor and BCR, as a result of n legislation, or by some new evidence of environmental contaminati extensive cleaning scheme will also be similarly modified when wa

statistically significant number of coals have been cleaned and a

one describing the results of the studies, the other including a

the initial results of the studies. Milestones in reporting for include a report in preparation on the state-of-the-art of fugiti emissions as they relate to the coal industry, as well as two fin

description of the analytical procedures used in the study.

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Sorg
S<sub>T</sub>, Pb, Fe
Spyr
           S<sub>T</sub>, As
Sorg
                                                 P.R.*, C1
           Spyr, Fe
As
           P.R.*, Cr, V, Na, Ti, P
Вe
                                                 V, Ti
Cd
                                                 Zn
           Ash, Be, V, Zn, Na, Si,
                                                 V
\mathtt{Cr}
             Al, Mg, Ti
           Ash, Zn, Na, Al, Ti
Cu
F
           Ash, Na, Al, Ti
                                                 K, Si, Mg
PЪ
                                                 Spyr, Fe
           Ash, Zn, Si, Al
Mn
                                                 Ca
Hg
Νi
Se
V
           Be, Cr, Na, Al, Ti
                                                 Be, Cr, Ti
Zn
           Ash, Cr, Cu, Mn, Na, K,
                                                 Cd
              Si, Al, Mg, Ti
Sb
           Ash, Be, Cr, Cu, F, V, Zn,
Na
             Si, Al, Mg, Ti
                                                 Ash, Si, Mg, P
K
           Zn, Si, Al, Mg, Ti
           Ash, Cr, Mn, Zn, Na, K,
                                                 Ash, F, K, Al, Mg
Si
             Al, Mg, Ti
           Ash, Cr, Cu, F, Mn, V, Zn,
Al
                                                 Ash, Si
             Na, K, Si, Mg, Ti
                                                 ST, Spyr, Pb
Fe
           S<sub>DVr</sub>, As
           Ash, Cr, Mn, Zn, Na, K
Mg
                                                 Ash, F, K, Si
              Si, Al, Ti
Ca
                                                 Mn
Τi
           Ash, Be, Cr, Cu, F, V,
                                                 Be, V
              Zn, Na, K, Si, Al, Mg
P
           P.R.*, Be
                                                 K
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Spyr, Fe

Si, Al, Mg, Ti

 s_{pyr}

 $\mathbf{S}_{\mathbf{T}}$

CĪ

*P.R. = Product Recovery

Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545 **ABSTRACT**

The aqueous drainage from coal piles and coal refuse dumps freq taminated with acids and a variety of trace elements and inorga The Los Alamos Scientific Laboratory is conducting research, jo by DOE/ECT and EPA, to assess the nature and magnitude of trace drainage from coals and coal preparation wastes, to identify th

of environmental concern in these effluents, and to define nece mental control technology for this form of environmental pollut emphasis of this program is on the laboratory assessment of env trol options for the drainages from high sulfur coals and coal presentation will review some of the accomplishments of this re to date, and discuss the various drainage control options avail industry.

INTRODUCTION

It has been well established that the drainage from coal refuse highly contaminated with trace or inorganic elements; however, about the quantities of undesirable elements that are released ronment from this source.(1) Development of the necessary contro for human and environmental protection requires quantitative ev extent and severity of the problem. LASL has been directed by assess the nature and magnitude of the trace elements in the dr preparation wastes, to identify the trace elements of greatest concern in these materials, and to evaluate required pollution

gy for this form of environmental contamination.

The research in this program is being conducted in several phas phase included studies of the structure and weathering and leac of the trace elements in selected samples of high sulfur refuse

element pollution of coal or refuse associated waters.

These investigations established the overall potential of these cause trace element contamination, and revealed the identities trace elements of concern in the refuse and coal pile effluents ion gathered on refuse and coal structure and environmental beh the basis for the present phase of the program, which involves development of control technology to lessen the environmental i

Research has now been started to identify suitable means to cor ment contamination of the drainages from high sulfur coal prepa These control techniques can be roughly divided into three cate immobilization or removal of contaminants prior to disposal of

EXPERIMENTAL

The coal preparation wastes used in this work were collected from three coal cleaning plants (designated Plants A, B and C) in the Illinois Basin. These samples of high sulfur coal refuse are typical of the wastes produced by cleing of the major coal types currently mined in the region. (2)

Both static and dynamic leaching experiments were conducted to evaluate the

environmental conditions and to test the effectiveness of potential environmental control methods. The static experiments were carried out by agitating known quantity of crushed refuse or composite (50 g) in the presence of a constant volume of distilled water (200 ml) for varying periods of time. In the dynamic or column leaching tests, a crushed sample (~ 1500 g) was packed int 70-cm-long by 4.6-cm-diam glass column and distilled water was continuously monitored through the column at a rate of 0.5 ml/min. The elemental composi

tions of the experimental leachates were determined by neutron activation anyses, atomic absorption spectrophotometry, optical emission spectroscopy and

havior of the trace elements in the Illinois Basin coal wastes under simulat

RESULTS AND DISCUSSION

Static and dynamic leaching experiments were performed to evaluate the trace

wet chemical methods. (2,3)

element behavior of Illinois Basin coal wastes under simulated weathering coditions. These experiments were done to provide information needed to prediquantitatively the trace element levels in the drainage from coal refuse dum or disposal areas and to identify those elements of environmental concern.

Perhaps the single most important characteristic of the high sulfur refuse materials during aqueous leaching is their pronounced tendency to rapidly produce acidic leachates. This is due to the oxidative degradation of the pyri

and marcasite present in the refuse. Acid formation is partially attenuated calcite or other neutralizing species in the refuse, but the leachates from Illinois Basin refuse samples that we studied nearly always had pH values in range of 2 to 4. These acid leachates are very efficient at dissolving or grading many of the mineral components of the refuse, and thus releasing the trace or minor elements associated with them.

Two types of trace element leachabilities were observed for all of the Illing Basin refuse samples. Because of their abundances in the refuse some element (such as Fe, Al, Ca, Mg) are released in relatively high absolute quantities Other, less abundant elements (for example, Ni, Co, Zn, Cu) are leached in a high proportion to the total of each present, although this may not be a lar amount in the absolute sense. The first group is highly concentrated in the

leachates, the second is highly leachable from the refuse.

safely assimilated by the environment. Application of the MEG r on the composition of refuse leachates obtained in this work, ar information in the literature, has revealed that nine elements, Ni, Zn, As and Cd are frequently present in potentially hazardou though these elements are not necessarily the only ones in the r that could conceivably be troublesome under all circumstances, t the priority elements that are receiving the greatest emphasis i work on environmental control technology. Two basic approaches to effect trace element controls are being this work. The first involves methods to treat newly produced c either at the preparation plant or during disposal to prevent th

provides a means for directly determining which or the contamina water solutions, such as those of interest here, exceed concentr

lease of trace elements from the disposal site. These technique fuse calcining, treatment of the refuse to remove acid forming of labile trace elements, and the application of adsorbents or atte to refuse disposal sites. The second approach concerns technique

abate the trace-element composition of already contaminated water from refuse dumps or disposal areas. Under consideration here a as alkaline neutralization, ion exchange, reverse osmosis, chala cation of selected adsorbents.

One of the more promising techniques under consideration to immediate hazardous elements in high sulfur coal refuse materials is calci fuse to high temperatures to produce an inert glass-like slag.

this area is directed both at identifying the chemical and physic brought about in the refuse structure as a result of the heat tr defining the consequent decreases in trace element mobilities.

An initial set of calcining experiments was performed using high preparation wastes from Plant B (Illinois Basin). The Sample wa crushing the refuse to -3/8 in. and calcining it in a quart, tub 850°C in air for 6 h. The calcined material, which had partiall was reground to -20 mesh for subsequent studies. The analysis of

composition of the calcined refuse sample showed that most of the retained in the calcined sample (Table I). A decrease in the co just a few volatile components in the refuse was noted. Of part was the loss of sulfur that occurred as a result of the calcinin original concentration of 13.4% S by weight in the non-calcined

described sample treatment yielded a product that contained only weight. From the standpoint of removal of the acid-forming cons

coal refuse, these results are quite remarkable since they show

in air at 800-850°C is a method that can substantially reduce the potential in the coal refuse wastes. Other volatile components trations were decreased by the calcining were Br, Pb, and Cd.

THE EFFECT OF CALCINING AT 800°C ON THE TRACE ELEMENT COMPOSITION OF AN ILLINOIS BASIN COAL REFUSE SAMPLE

<u>Element^a</u>	Uncalcined Refuse	
A1 (%)	5.9	
Mn	144	
Fe (%)	11.0	
Со	30	

Ni

Cu

Zn

Pb

S (%)

Cd (ppb)

Calcin Refus

11.5

19.0

70

110

73

296

290

12

1.1

191

71

35

149

400

34

Another set of calcining and leaching experiments was performed to determine optimum heat treatment conditions necessary to chemically immobilize the pot tially toxic trace elements in the refuse matrix. These experiments were pe formed using high sulfur coal preparation wastes from Plants B and C (Illino Basin). The wastes were ground to -20 mesh and calcined in air at 600° C, 80° C 1000° C, and 1200° C for 2 h. The calcined residues were then statically lead (stirred with distilled H2O) for a period of 48 h using a ratio of 4 mg H2O I g of calcined refuse, and pHs and total dissolved solids determined. The data are summarized in Table II. It is seen that heating to 600°C and higher results in a leachate with an elevated pH -- this is a consequence of the re moval of the volatile, acid-forming sulfur component and is consistent with experimental data on sulfur volatilization. Calcining at 1000°C also result in a strong decrease in the leachate's total dissolved solids. Physically, samples calcined at 1000°C showed signs of sintering. It appears, based on

^aElemental compositions reported as ppm unless otherwise indicated.

13.4

Sample Source	Calcining Temp., C	Sample Wt. Loss, %	Leachate pH
Plant C	Uncalcined		2.9
Plant C	600	23	6.6
Plant C	800	23	6.2
Plant C	1000	23	7.8
Plant C	1200	23	8
Plant B	Uncalcined		1.8 ^b
Plant B	1000	38	7.0

OF HIGH SULLOW WELLOSE

bleachate pH measured after 4.4 h of leaching.

aStatic leaching of 20 g of crushed refuse with $100~\mathrm{m}^2$ of water

illustrated by the data from a comparison leaching experiment in of the refuse samples (Plant C) that had been calcined at 1966 (The calcined and uncalcined refuse samples listed in the table to jected to static leaching for 48 h. It is seen from the internal table that calcining has essentially eliminated the acid generat

of the refuse samples and that the TDS contents of the resulting substantially reduced. More important is the fact that the constant the abbreviated group of toxic elements listed have been reduced cined refuse leachates by about two orders of magnitude over the in the leachates produced from the raw refuse materials.

Several methods are being considered to treat coal refuse during prevent the release of trace contaminants during subsequent was to

ing or leaching by surface or ground water. These include codis refuse material with neutralizing agents or trace element adsorbe application of water tight sealants to all or parts of the waste

Especially promising among these techniques is the codisposal of materials with alkaline agents such as lime. In one set of experi example, powdered lime in varying amounts (3 to 50 g) was slurrie of distilled water with -3/8 in. high-sulfur coal refuse (530 g.

TRACE ELEMENT LEACHABILITY OF A PLANT C COAL REFUSE SAMPLE CANCINED AT 1000°C FOR 2 H.a **Uncalcined** Refuse

2.9

.6

100

600

2.8

dHa

A1

Fe

Zn

TDS (%)

Calc

Ref

7.

Fe	600	<.
Mn	5.8	
Co	2.8	<.
Ni	4.7	<.

aResults from static leaching of 50 g of crushed refuse material with 200 ml of water for 48 h. ^bLeachate compositions reported as ppm unless otherwise noted.

to -3/8 in. particles. Four different lime concentrations were employed: 1.5, 3 and 10 wt %. In addition, a control refuse sample that had not been

lime-treated was also incorporated into this study for comparison purposes. Column leaching experiments were conducted with about 500 g of each of the samples to determine the effects of the lime additions. The refuse mixture were packed into pyrex columns 25 cm long by 5 cm diameter and subsequently

leached with distilled water at a flow rate of 0.5 ml/min until more than 4 of water had been passed through the refuse beds. The compositions of the ates after about 300 ml of water had passed through the columns containing

refuse are given in Table IV.

Although the data are not listed in Table IV, the leaching experiments show that the addition of 0.5 and 1.5 wt % lime to the acid refuse had only a sm

influence on leachate pH and trace element concentration because the acid neutralization provided by these amounts of lime was overwhelmed by the acid generating capability of the refuse. The additions of 3 and 10 wt % of the

on the other hand (Table IV), did indeed effectively counteract the acid pro

	•	CONTENTS OF OS.	
	·	Untreated Refuse Control	Refuse + 3% Lime
д _Н ф)	2	7
	i (%)	4	0.4
ΓA		720	<0.6
Fe		7800	40
	· ·		

Re'

1

0.3

0.5

0.1

Fe	7800
Mn	22
Со	12
Ni	18
Zn	29

aresults from column leaching experiments with Illinois Basin P (see text). ^bLeachate compositions are reported as ppm unless otherwise note

The system containing 3 wt % lime is especially interesting beca of 7 was maintained for nearly the entire duration of the leach

(until 4.2 & had been passed through the column). TDS values for lime combination were also very respectable (ranging downward fr stantially to the dissolved solids content of the solution.

wt %) especially considering that the dissolution of the lime it Another potentially fruitful way to retain the leachable contami

refuse disposal site is to intermix the acid coal wastes with su of trace element attenuating agents. An example of one of the s in this area will illustrate the potential utility of the method In this experiment, acidic coal refuse leachates were equilibrat

solid sorbent materials to evaluate their trace element attenuat prior to using these agents in codisposal experiments. The soli illite, montmorillonite, and kaolinite clays; a sample of scrubb cipitator ash and two samples of bottom ash, each from different an acid drainage treatment sludge, and a clay wish

leachate pH elevation, and attenuation of 13 trace elements that have been identified as being of greatest environmental concern in the Illinois Basi refuse effluents. The data have been isolated into different sections in VI to draw attention to some of the pertinent features. For example, since solubilities of Fe^{+3} and Al^{+3} are very sensitive to pH in acidic solutions sorbents that are most effective in elevating the pH above a value of 5 are most effective in decreasing the concentrations of Fe and Al. In Table VI the pH, Fe, and Al results are grouped together it is seen that 7 of the 1

TABLE V

THE ATTENUATION OF TRACE ELEMENTS IN COAL REFUSE LEACHATES BY VARIOUS ATTENUATING AGENTS^a

Fly Ash

9.6

0.6

0.2

Scrubber

Sludge

7.3

< 0.2

< 0.1

Mn	4	2.2	0.04	C
Со	1.9	0.7	0.1	(
Ni	2.6	0.8	<0.05	d
Zn	1.0	0.6	0.02	C
		·		

aResults from interaction of 50 g of attenuating agent with 150 ml of con-

leachate for 15 h.

sorbents tested are very effective.

Untreated

Leachate Control

2.6

10

107

^dHa

A1

Fe

DLeachate compositions reported as ppm.

	Hd	Z	۲
	EVATE S IN	2	<u>.</u>
	(a) EL LEMENT	F4	ָרָי ב
	S TO ACE E CHATE	C	प्रम
	RBENTS TY TR/ E LEAG	٥١	<u>_</u>
H	EN SORI	ပ္ပါ	9
TABLE VI	F ELEV TEEN P COAL	Zn	EEE
 -	TIES O E THIR BASIN	Mn 2	EEE
	COMPARISON OF CAPABILITIES OF ELEVEN SORBENTS TO (a) ELEVATE PH AND (b) ATTENUATE THIRTEEN PRIORITY TRACE ELEMENTS IN ILLINOIS BASIN COAL REFUSE LEACHATE	pH Fo Al Ni Mn Zn Co Cr Cu F Cd Na	CC
	(b) AT	2	EEE
	ARISON AND	Fo	EEE
	WOO	Hd	EEE
		SORBENT	c 0,

4

Д

Д

GG

Д

μ

GG	GG
FF	GG
Ъ	gg
gg	GG
EEE	GG
BEE	GG
CC	999
EEE	ECE
EEE	EEE
999	333

EEE

EFE GG

Treatment Sludge

Illite

CaCO, AMD

CaCO,

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GG	
मृभ	
CC	
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gg	
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GG	טט
CG	S.
EEE	EEE
DEE F	EEE

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	EEE	
	GG	
	GG	
	SEE	
	BEE	

GG	म	स
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स्स	ম	വ
0	GG	GG
GG	GG	FF
GG	GG	GG
BEE	CG	D.
GG	gg	नुग
GG	યા	EEE
EBE	ECE	333
EBE	ECE	BOE
Precipitator Ash	Montmorillonite	Bottom Ash

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SO, Scrubber Sludge

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Bottom Slag

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Exa Exa

Kaolinite

C

Trees Co

osmosis, chelation and biological treatment.

Untreated Leachate Control

1.1

0.5

18

indicated pH was achieved.

dHa

Αī

TDS (%)

While it is well known that alkaline neutralization is very effective in c trolling the acid and overall salt compositions of mine waste waters, the gree of control that this method exerts over some of the more highly leach able toxic trace elements remains to be established. (1) Elaboration of the latter point is the basis for one of the studies now being conducted in th area.

TABLE VII ALKALINE NEUTRALIZATION OF CONTAMINATED COAL REFUSE DRAINAGEA

Lye

3.4

< 0.2

6

Limestone

7.1

3.2

< 0.2

Lim

6.

3.

< 0.

One of the most promising of these control techniques, alkaline neutraliza tion, is currently used extensively to treat acid drainage from coal mines

Fe	820	0.06	0.3	0.
Mn	3.6	0.07	6.4	1.
Со	2.0	0.05	1.0	0.
Ni	3.2	0.05	1.0	0.
Zn	3.9	0.02	0.1	0.

^aResults from addition of alkaline agent to 12 of control leachate until

^bLeachate compositions reported as ppm unless otherwise indicated.

ments are summarized in Table VII. Examination of Table VII shows that neutralization is an effective te for decreasing trace element concentrations in refuse waste water. The and Fe contents of the treated solutions are within acceptable limits the 1977 EPA effluent limitation guidelines for coal preparation plant

trace element contents of them were measured. The results of these e

(Fe $\leq 3.5 \, \mu \text{g/ml}$ averaged for 30 days, pH 6-9). Mn, however exceeds the able level of 2.5-3 µg/ml (averaged for 30 days) in the limestone case however, this was shown to be due to traces of Mn in the limestone use neutralization experiments. Further work in the area of alkaline neut of refuse drainage involves its application to more highly contaminate to investigate coprecipitation phenomenon, and the scale up of the pro

SUMMARY The purpose of this paper has been to present an overview of research at the Los Alamos Scientific Laboratory to investigate experimentally the more attractive options for controlling trace element contaminatio refuse drainages. The control methods under consideration include che and physical methods to immobilize or remove undesirable contaminants refuse disposal, the treatment of refuse disposal sites with attenuati or sealants to prevent the discharge of contaminated water, and the di treatment of refuse drainage as it emerges from the refuse disposal si

trace element contamination of refuse dump drainage.

initial quantitative results from these laboratory studies suggest tha techniques being considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible for effectively considered are technically feasible

more life-like circumstances.

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Abstract

The cross section for particle collisions with an isolated magnetized fiber in air and water is given as a

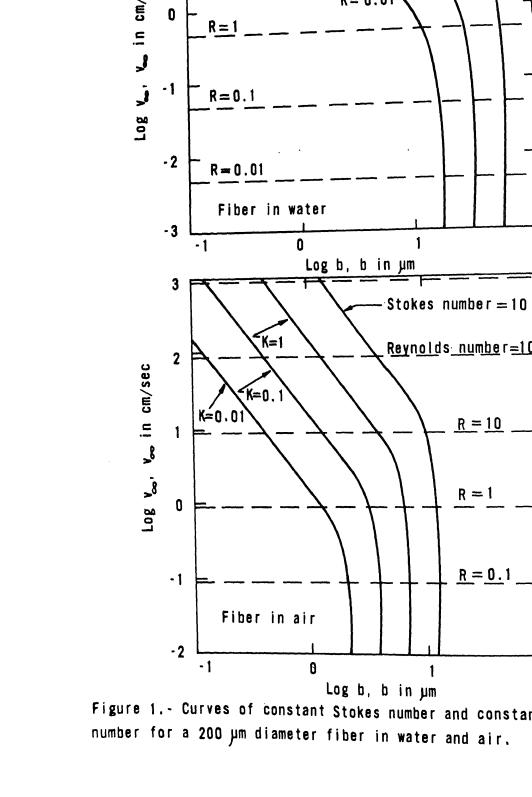
function of the physical parameters of the filter system. Two models for using the cross section to predict real filter efficiency are discussed. The analysis of particle in air shows a strong dependence of cross section on particle inertia and gravity and pronounced maxima in the cross section at small particle radii, features which are not present in liquids. The cross section in air is especiall sensitive to particle size at small particle radii and to the free stream velocity. The cross section in air is reasonably large for a range of conditions, which supports

the view that economically practical applications of magnetic filters in air-particle separations may be possible.

separation method was subsequently used for commercia tical filtration of magnetic impurities from Kaolin A number of other practical applications were pointed Oberteuffer(5) and recently many specific filtration in air and liquid streams, including coal related ap have been discussed. (6) The basic physical idea underlying the operation gradient type devices is simple: If a ferromagnetic placed in a magnetic field it becomes magnetized and Many thin fibers placed transversely to netic field form a fibrous filter which, although su porous to allow a relatively free flow of fluid, cap carries a substantial load of magnetic impurities. Work carried out at METC has been concerned with standing of the basic physical elements of the filtr These studies have been on the dynamics of ture of particles by an isolated fiber and by a fibe interior of a regular lattice of fibers. Here we su the results and discuss their application to the ana the performance of real filters. We consider two di models for calculating the filter efficiency, the is model and regular lattice model. The cross section for capture has been calculat isolated fiber and for a fiber in the interior of a fibers. (7) These calculations show that for a highl filter, say fiber spacings greater than eight fiber cross section for the isolated fiber and a fiber in are approximately equal. This does not mean that th interference effects in porous filters, for even tho cross sections may be nearly equal in the two cases, of the shadows (in particle density) cast by fibers affect the efficiency of the filter as a whole. The fiber model neglects entirely the interference, incl shadows, of neighboring fibers, whereas the lattice siders the fibers as a coherent array and accounts f effect of the lattice as a whole on particle traject isolated fiber model gives an optimistic estimate of ciency of a real filter whereas the lattice model sh vide a low estimate. We discuss first the isolated and present functional dependence of the clean fiber section on the filter parameters. The regular latti discussed in section 3. Isolated Fiber Model In a filter with fiber perpendicular to the str the capture distance, x_{c} , is the maximum value of th impact parameter for which the particle trajectory i

separation to filter fine particles was stimulated by of Kolm et al.(1,2) The so-called high gradient magn

separacion d, one average number of cargers (iii) is $1/\alpha^2$. If the fibers act independently the probabilit of capture for a particle traveling a depth dy in the direction of the stream is $-2x_c dy/\alpha^2$. The probable chang particle density, dn, is $2x_c n dy/\alpha^2$ and it follows that t efficiency of a filter of depth y is $1 - \exp(-2x_cy/\alpha^2)$. These hypotheses explicitly neglect the shadows, i.e., neglect the nonuniformities in particle density in the transverse direction caused by capture of particles from the stream. For particles greater than 1 µm we do not expect that diffusion of particles into the shadows is sufficiently rapid to maintain the assumed transverse un formity. In the isolated fiber model the cross section is calculated in the approximation which neglects the effec of neighboring fibers. The interference effects are acc for by introducing an empirical factor, say k, in the ex nent of the efficiency formula. If the fibers are orien in random directions with respect to the magnetic field, only that fraction of the fibers perpendicular to the fi should be counted, which correction may also be absorbed in the empirical factor k. If the theory is used to represent a filter operating over a period of time, the corrections to the cross section for buildup of particle on the fibers given by Luborsky and Drummond (8) and Watson (9) should be applied. Even though the empirical correction required to br calculated and observed efficiencies into agreement is q large, (8,10,11,12) the isolated fiber model has been use for identifying the significant physical parameters and for giving roughly correct functional dependence of effi ciency on the parameters. The isolated fiber cross section has been calculate by Watson $^{(13)}$ and Luborsky $^{(4)}$ for inertialess particles and by Lawson et al. (14) for particles with inertia. Usually, particle inertia is negligible for filtration o liquids and significant for filtration of gases, at leas for the size range usually considered in magnetic separa A well known order of magnitude argument shows that the onset of inertial effects should be expected at stokes number, K, greater than O.l. However, even though the shapes of particle trajectories are in fact affected by inertia(14,15) at K > 0.1, the net effect of inertia on capture cross section is small up to K = 1 for cross sec greater than a fiber diameter. An idea of the range of particle size and free stre velocity for which particle inertia is negligible may be obtained from figure 1. To the left of the K = 1 curves particle inertia is negligible in the computation of cro sections for cross sections greater than a fiber diamete for a fibor diameter of 200 um



isolated fiber. Below R = 10, potential flow misreprese fluid field, but for cross sections greater than a fiber meter the error incurred by this approximation may not b excessive. The isolated fiber cross section has been calculate a broad range of conditions which include filtration in For conditions such that particle inertia and the gravit tional force are negligible, the cross section depends single dimensionless parameter. (13) This parameter is t ratio of a magnetic quantity, vm, with the dimensions of velocity and the free stream velocity v_∞ . Increasing v_m either by increasing v_m or decreasing v_∞ , increases the section. When particle inertia and the gravitational forces significant, the cross section is a function of three disionless parameters, (14,15) $v_{\infty}/v_{\rm T}$, the Stokes number and v_m/v_T , where v_m is the terminal velocity of a particle f parallel to the free stream. The expressions for the si ficant parameters are

n, indicates whether fluid viscosity is significant in d mining the flow field. For Reynolds number greater than potential flow, which neglects fluid viscosity, is proba an adequate representation of the flow on the front side

$$v_{T} = v_{\infty} + \frac{2\rho_{p}b^{2}g(\rho_{p}-\rho_{f})}{9\eta}$$
,
 $v_{m} = \frac{2\chi Bb^{2}M}{9(1+\chi/3)\eta a}$,

$$K = \frac{2b^2 \rho_p v_T}{9\eta a} .$$

There are nine physical quantities involved here, the pa

 ρ_D , mass density,

b, radius,

properties,

X, magnetic susceptibility,

the fluid characteristics,

ρf, mass density,

B, the external magnetic field strength.

The dependence of cross section on the dimensional parameters v_m/v_T , K and v_{∞}/v_T is shown in figures 2 and there have been observations of trajectories and cross tions for particles in air(15) which are in agreement cross sections shown here, which provides a check on theory for a small range of the parameters considered theory for a small range of the parameters 4 to 11 as

The cross section is shown in figures 4 to 11 as of the physical parameters B, b and v_{∞} . The cross section for particles in air and water for low, moderate particle susceptibility. As discussed above, in the fiber model, the cross section is used to calculate the ciency from the expression

where $X_c = x_c/a$ is the cross section in units of the diameter. Taking k = 1 neglects fiber orientation an ference effects entirely and provides an upper bound

efficiency = 1 - exp-
$$\left(\frac{k2X_cay}{\alpha^2}\right)$$
,

efficiency of a real filter. In section 4 we will dicertain prominent features of the cross section curve first we consider the lattice model of a filter.

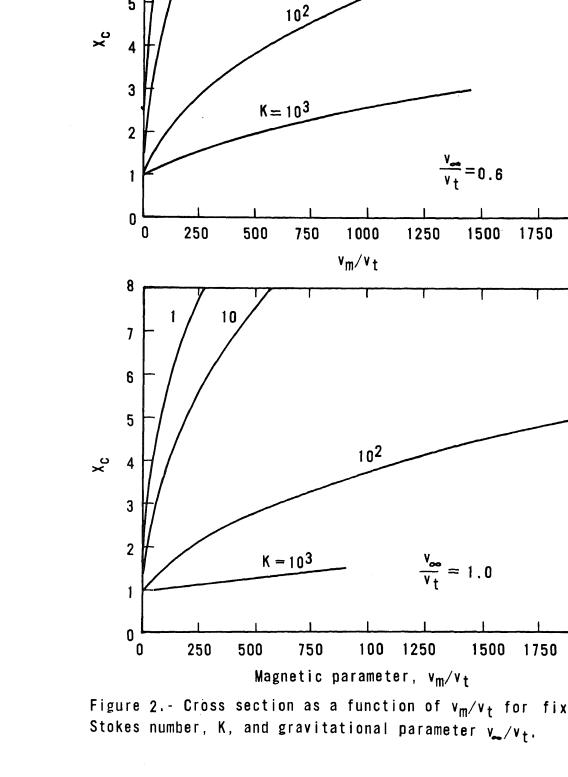
3. Regular lattice of Fibers.

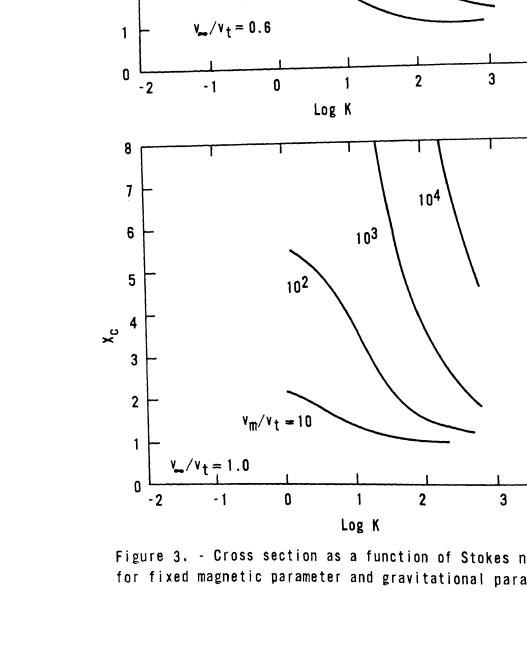
We give now a brief description of the regular land the results of the calculation of trajectories an section. The details of the analysis and full account results are given in reference 7. The lattice consist parallel circular fibers with fiber axes perpendicular magnetic field. The fluid flow and gravitational fied parallel and directed oppositely to the magnetic field.

rectangular and rhombic lattices have been studied.

The external magnetic field magnetizes the fiber each fiber acquires a uniform magnetic moment per unilength in the direction of the magnetic field. The refield is the external field plus the field caused by netized fibers. The fluid field is the sum of the unflow and the fluid disturbances caused by the circular we have developed analytical expressions for the results.

fields which represent a lattice with its longest din in the direction of the field. From these expression forces on a magnetic particle in the interior of a latest contract of the interior of the latest contract contra





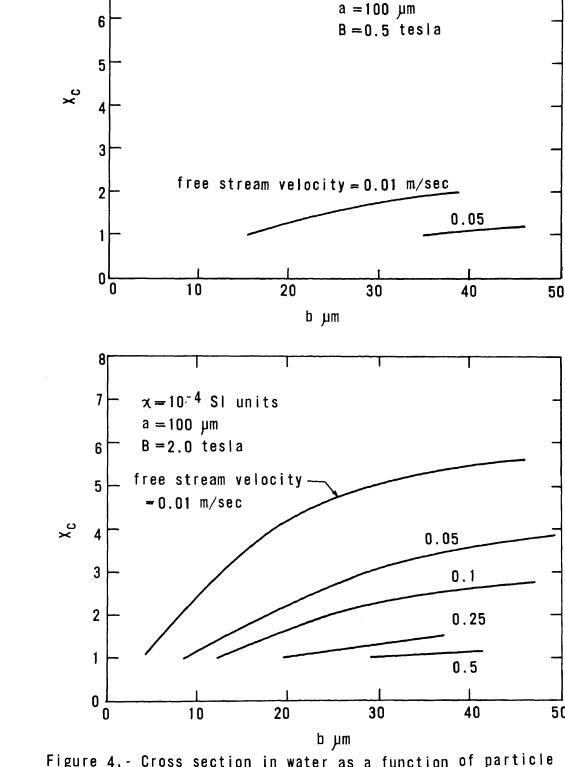
 $v_m/v_t = 10$

5

3

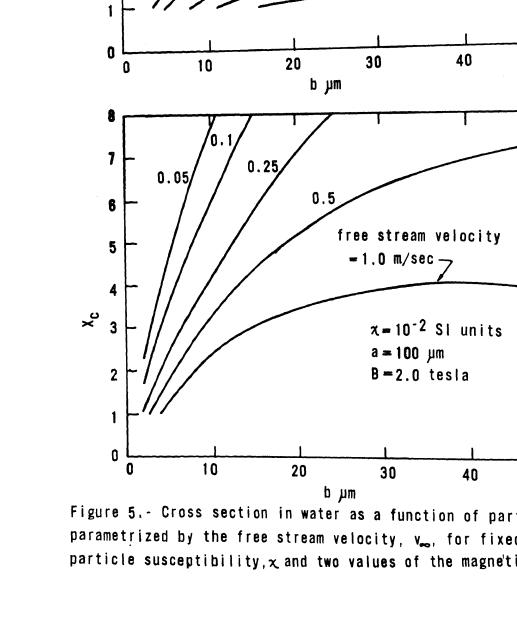
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×° 4



50 Figure 4. - Cross section in water as a function of particle

narametrized by the free stream velocity, v., for fixed low



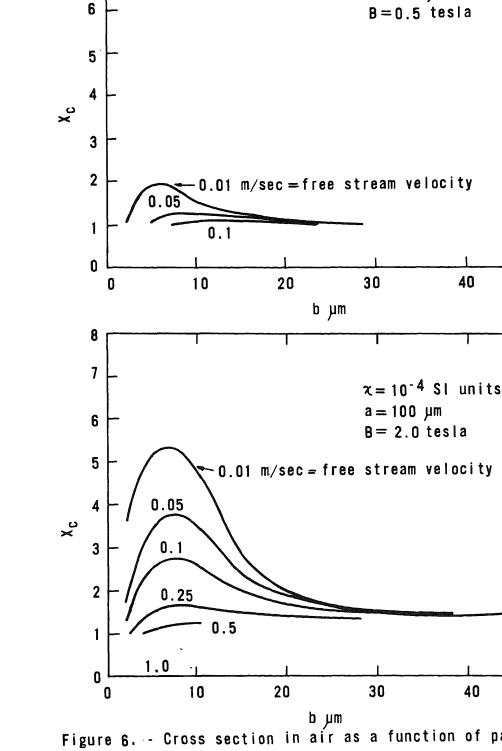
2

free stream velocity

0.5

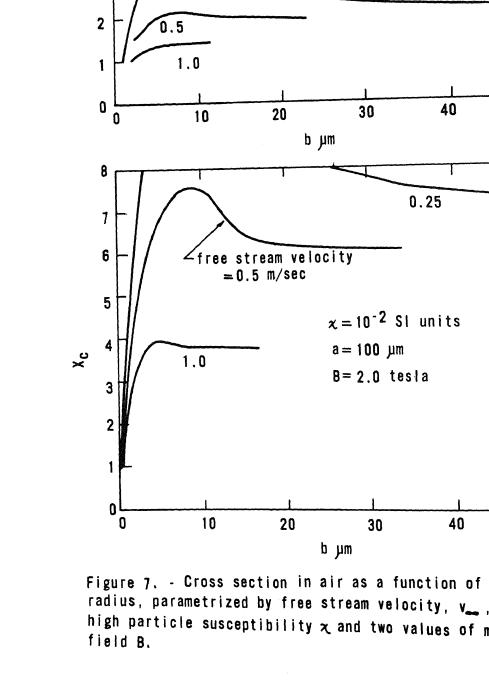
1.0

= 0.25 m/sec



 $a = 100 \mu m$

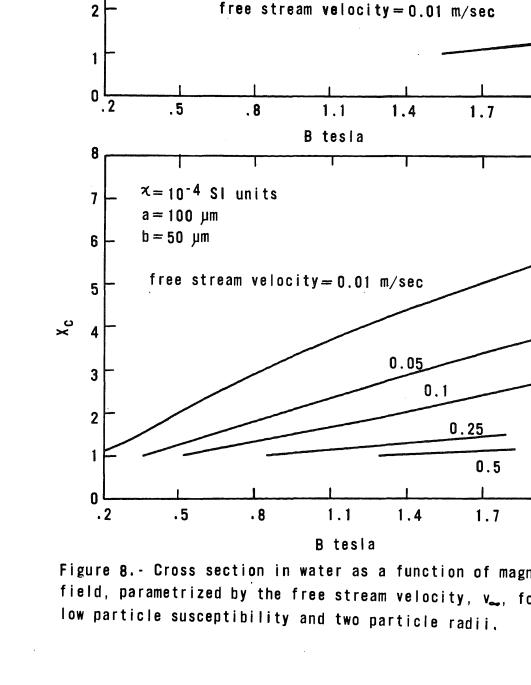
Figure 6. - Cross section in air as a function of part

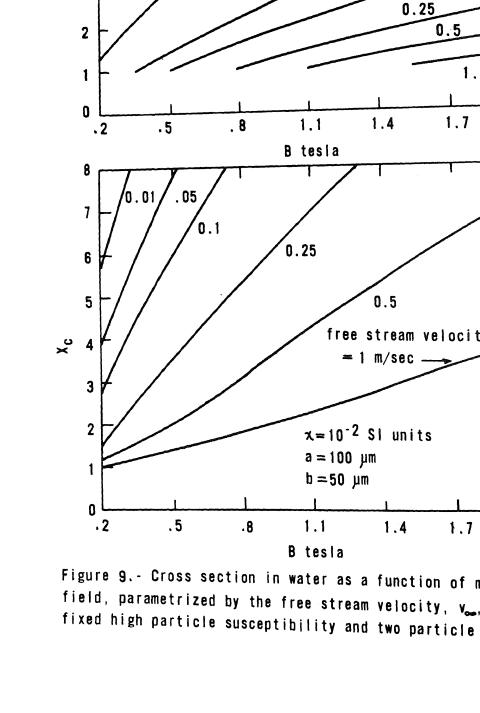


3

0.25

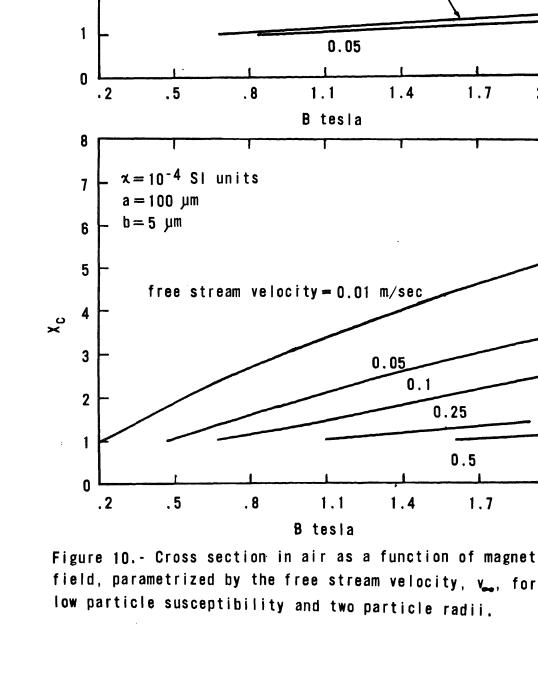
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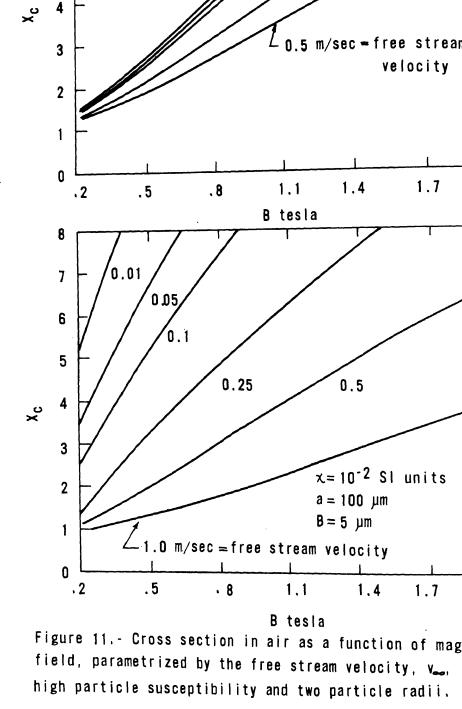


0.05

0.1



free stream velocity = 0.01



1.7

1.7

Figure 11. - Cross section in air as a function of mag field, parametrized by the free stream velocity, $\mathbf{v}_{\bullet\bullet}$, high particle susceptibility and two particle radii.

trajectories are separated into those which intersect th fibers and those which do not. Trajectories which enter an upper cell boundary and do not get captured will leav that cell and enter the cell below. Since this pattern repeated these trajectories will not intersect any of th fibers below. Thus, excape channels are formed which pe particles to pass through the filter. The width of the depends on v_m/v_T and can be made as narrow as one please increasing $v_{m}^{-}/v_{m}^{-},$ e.g. by increasing the magnetic field. One sees at this point an essential difference betw the filter efficiencies of the isolated fiber and the la models. Assuming a horizontally uniform distribution of cles entering the lattice the number of particles passin through the filter is proportional to the width of the e channel, which is $\alpha - 2x_c$ in the case of the rectangular tice. The filter efficiency is thus, simply, $2x_c/\alpha$. A result holds for the rhombic lattice. As noted above th limit $2x_{\alpha}/\alpha = 1$, which implies an impenetrable fiber lay can be obtained for sufficiently large v_m/v_T . It is not worthy that the lattice efficiency is independent of fil depth in contradistinction to the exponential dependence obtained from the isolated fiber model. We expect that the lattice model gives a low estima of real filter efficiency. The regularity and complete coherence of fibers in the lattice probably includes the effects of shadows rather too strongly, whereas, the iso fiber viewpoint neglects completely the fiber shadows. better description would seem to lie somewhere between t models. 4. Discussion The dependence of the cross section on the paramete the system is shown in figures 4 to 11. The cross secti used to compute the efficiency of a clean porous filter

The equation has been integrated in the approximation wh neglects particle inertia, and trajectories and cross se have been obtained. The cross section is shown in figur as a function of v_m/v_T for a fixed horizontal distance be fibers and different spacings in the vertical direction both rectangular and rhombic lattices. Multiplication o cross section shown in figure 12 by $\alpha/2a$, where a is the radius, gives the cross section in units of fiber diamet allows a comparison with the isolated fiber cross section for fiber separations $\alpha/a \ge 8$, the isolated fiber and the in a lattice cross section are not greatly different.

Particle trajectories in the rhombic and rectangula

lattice are shown in figure 13. Because of the periodic of the force field the pattern of trajectories found in cell will be repeated throughout the lattice. It is see

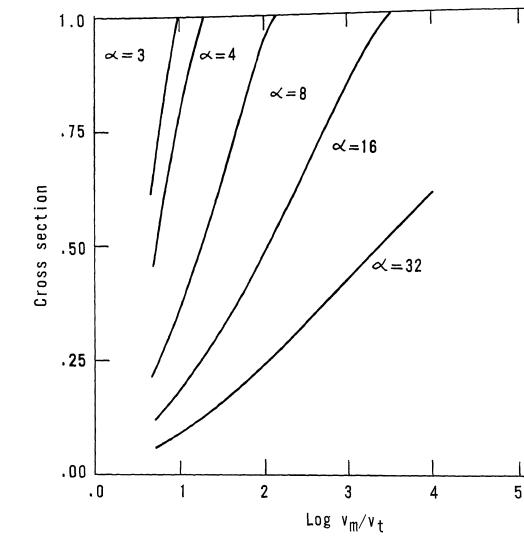


Figure 12.- Cross section for a fiber in rectangular I function of magnetic parameter with horizontal distance fibers fixed at $\beta = 8$.

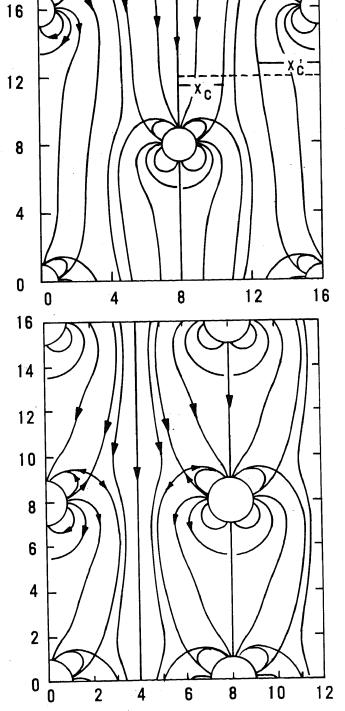


Figure 13. - Particle trajectories in 8x8 square and rhombic lattices showing escape channels.

of the gravitational force. For example, if $v_{\infty}/v_{\mathrm{T}}$ = 1 is no gravitational effect and $v_{\infty}/v_{\mathrm{T}}$ = 0 corresponds to particle falling past a fiber in still fluid. The cross section as a function of Stokes number, metrized by the magnetic parameter, is shown in figure One sees the strong decrease of cross section with Stol number at large Stokes number. This behavior makes it cult to obtain large cross sections in air at high free However, at moderate and low velocities i velocities. not hard to obtain rather large cross sections. For e in air for a moderate particle susceptibility, $\chi = 10^$ units, magnetic field B = 1.0 tesla, particle radius 1 and iron fibers of radius a = 100 μm , we obtain from t expression on page 4, v_m = 18 m/sec. Then if v_∞ = 0.2 we have v_m/v_T = 54, v_∞/v_T = 0.6 and K = 47, the latter being in the inertial range. Referring to the upper g in figure 3 (or figure 2) we obtain a cross section of two fiber diameters. Figures 2 and 3 and the numerical example illustr point which has already been appreciated, for example, Gooding et al. (11): The flow velocity is an especially parameter in the magnetic filtration of air. It is of also important in liquids, but in air higher velocitie generally required and the cross section decreases wit creasing velocity by virtue of a decrease in the magne parameter and an increase in Stokes number. Whereas, inertialess condition, typically realized in liquids, Stokes number dependence is absent. Figures 4 to 7 show, for air and water, the depen cross section on the particle radius. It is often not high gradient magnetic separation is especially suited filtration of fine particles. Although this method ma better than others one nevertheless notes that in wate monotonic increase of cross section with particle size the capture of the larger particles. In air, where inertia is important, both v_m/v_m an increase with increasing b and the competing effects r in pronounced maxima in the cross section shown in fig 6 and 7. Roughly speaking, the maxima are caused by t increase in $v_m/v_{\overline{m}}$ with b at small b and the increase i minal velocity and particle inertia having a dominant at high b and bringing the cross section down. The monotonic increase of cross section with the field shown in figures 8 to 11 is simply due to the in in the magnetic parameter when the other parameters ar

magnitude of the parameter $v_{\infty}/v_{\mathrm{T}}$ is a measure of the e.

The theoretical cross section for the collision of cles with magnetized fibers is given as a function of th physical parameters of the filter system. The cross sec for particles in liquid is well known and the graphs for water given here show only additional details of the fur dependence on the parameters. The relatively large cros sections found in liquid have encouraged the investigati of practical applications. The results presented here f particles in air extend existing results. The cross sec are reasonably large for an interesting range of conditi which supports the view that filtration of fine particle in air may be economically practical.

5. Summary

Unfortunately it is not possible, at this time, to predict with reasonable accuracy the efficiency of a rea filter with the aid of the isolated fiber cross section. suggest that the interference effects in real filters ar very important and are not accounted for correctly either the isolated fiber model or the lattice model. Neverthe the isolated fiber cross section has been a reliable ind of the qualitative behavior of real filters. In air the cation is that the fiber cross section and hence the fil efficiency is very sensitive to free stream velocity, ar cross sections will be relatively low for applications v require moderate magnetic fields and free stream velocit 1 m/sec and larger. Of course filter efficiency can alw be increased by increasing the density of fibers and dep the filter but only at the expense of pressure drop acro the filter. The analysis in air also shows maxima in the cross section at about 10 um which are not present in 1 The maxima are very pronounced at low velocities and ter

disappear as the free stream velocity is increased.

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INTRODUCTION

20-year period with coal serving as the primary fuel for electrical g

Coal production is expected to increase significantly over the

tion, replacing dwindling supplies of domestic oil and gas, and reduce dependence on expensive imported oil and gas. Coal production will a increase to meet the needs of the emerging gasification and liquefact industries. The increased tonnage will be from new mines or from exp of existing mines; many of these mines will be (or are) located in confields east of the 100th meridian. This line, lying east of the North Dakota lignite field and west of the Texas coal fields, roughly divide country into two regions: a western region of low-sulfur coal where refine usually less than 26 inches/year, and an eastern region where rain generally exceeds 26 inches/year and most of the coal (lignite except well as the rocks overlying the coal, often has a relatively high sulface.

content. Sulfur in the eastern region is primarily in the form of ir pyrite. Mining eastern region coals exposes the pyrite to oxidation, in ferrous sulfates which produce acid upon hydrolysis. The acidic w or is pumped from the mine and, unless effectively treated, leads to environmental degradation of streams and lakes within the watershed a

In early FY 76 a program was begun at Argonne National Laborat

(ANL) to evaluate technologies for controlling the environmental impare effluents resulting from the surface mining of coal. The program is performed for the Department of Energy's Division of Environmental Controlling (DOE-ECT) as part of ECT's overall mandate to assess the eness of methods for controlling pollutant emissions from energy extra conversion, and utilization processes. Initial support for this study "pass-through" funding from the U.S. Environmental Protection Agency current support comes from DOE-ECT.

potential health hazards from a polluted drinking water supply.

This program has a twofold purpose which is related in part to interests of its two federal sponsors. The overall issue addressed be sponsors is the need to satisfy increased coal demand in an environment acceptable manner. Each sponsor, however, has particular objectives is interested in an evaluation of the efficacy and practicability of

is interested in an evaluation of the efficacy and practicability of mine effluent control options currently in use, an identification of technology needs, and recommendations for research. The EPA is interin an assessment of the validity of the recently promulgated effluent

in an assessment of the validity of the recently promulgated effluent lines for the coal mining industry, with this assessment emphasizing and climatic variation impacts on effluent quantity and quality. A plan was outlined to: (1) project future coal production levels to the coal production of the coal production levels to the coal production of the coal production data at the coal production.

basis for national judgments on the practicability of present and anti environmental standards.

The results of this program are providing data for federal and industrial decision-makers concerned with: (1) developing criteria for choosing the "best" environmental control option; (2) policy decisions involved in the siting of future coal facilities; and (3) establishing

agencies.

The program interacts with the National Coal Association, 15 co companies, 12 universities, and 10 state and federal regulatory/resear

PROGRAM PLAN

This program is focused on the assessment of alternate control

nologies that show promise for environmentally safe handling of efflue and wastes from strip mining operations in the eastern region (east of

meridian) coal fields through the end of the century. The program has divided into five tasks, and a unit operations master plan developed w shows the interrelationship of the tasks (Fig. 1): TASK 1 - FUTURE COAL PRODUCTION SCENARIOS

AND CASE STUDY SITE SELECTION In this effort ANL estimated future coal production levels thro year 2000 and identified areas east of the 100th meridian where surfac coal production is expected to increase. A series of maps was produced

each state's coal fields, active mines producing over 200,000 tons per and proposed new mine openings. A series of computer-drawn maps of each state's coal reserves also was completed; these maps show total, surface and deep minable reserves for each county where data is available. Fro maps and from contacts with the National Coal Association, industry sou and the U.S. Bureau of Mines, twenty-one areas were chosen as the most places for increased production. Mines were selected for each area who typified local coal field conditions. Permission was obtained from mir company officials to use the mines as case study sites from which data be gathered regarding the volume and character of mine effluent dischar

TASK 2 - MINE DRAINAGE GEOCHEMISTRY

An intensive sampling program was developed to determine the vol and characteristics of mine effluents at each of the twenty-one case st

mines. All mines were coded to shield their identity. Consultants und Argonne supervision conducted sampling activities; samples were obtained the mine pit discharge point before any treatment and at the treatment charge point, thus obtaining a measure of the treatment efficiency. Sa

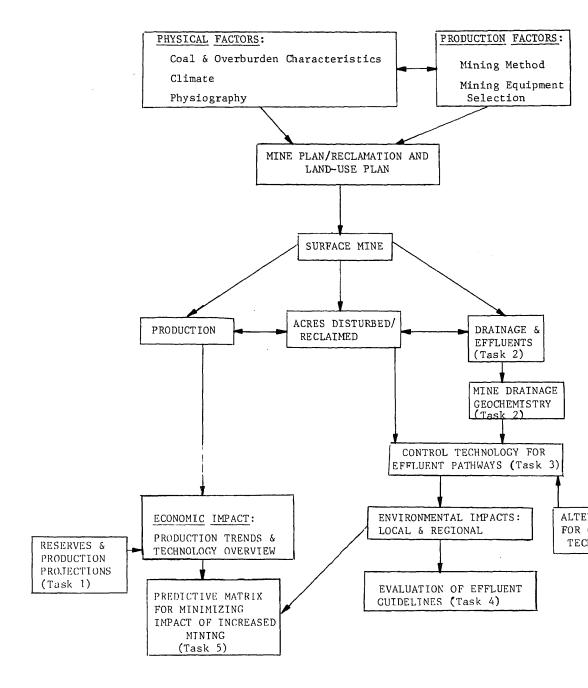


Fig. 1. Unit Operations Master Plan

analyzed included:

Mercury
Vanadium
Molybdenum
Cobalt
Nickel
Chromium
Lead
Copper
Zinc

The overburden was sampled and analyzed for major, minor, and elements, and forms of sulfur. Coals were sampled and underwent pro and ultimate analyses in addition to the same types of analyses perf on the overburden. Acid potential (derived from pyritic sulfur) and

Trace element analysis was performed every three months.

The field sampling phase has been completed and the data are

reviewed and analyzed. Argonne is analyzing the sample data and ass the environmental impacts and pollution potential for each site. The ment, coupled with the information relative to the increased coal prand control technology options, will provide the baseline data for a

Aluminum

Chloride

Fluoride

Strontium

Magnesium

Potassium

E1e

Ammonia

Sulfate

on the potential environmental impacts related to increased surface through the end of the century. Figure 2 summarizes the various oper for Task 2.

neutralization potential were also determined.

Conductivity

Dissolved oxygen

Acidity/alkalinity

Total dissolved solids

Total suspended solids

рΗ

Iron

Sodium

TASK 3 - CONTROL TECHNOLOGY ASSESSMENT

Mine effluent quality is being examined before and after treat to provide a measure of the effectiveness of the treatment process. technology cost data are being obtained whenever possible. Process products are being identified and characterized, and the economics of disposal/reclamation are being considered. The environmental impact waste products generated by the various treatment process and select

alternative processes are being studied. Figure 3 indicates the identity operations for control technology assessment at surface coal management system for computer storage of the data genunder this program has been selected and implemented. All relevant storage and retrieval systems were reviewed, and System 2000 was selected.

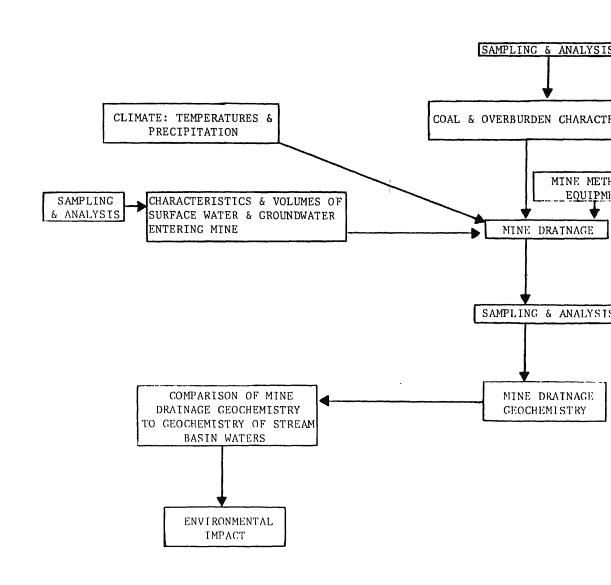
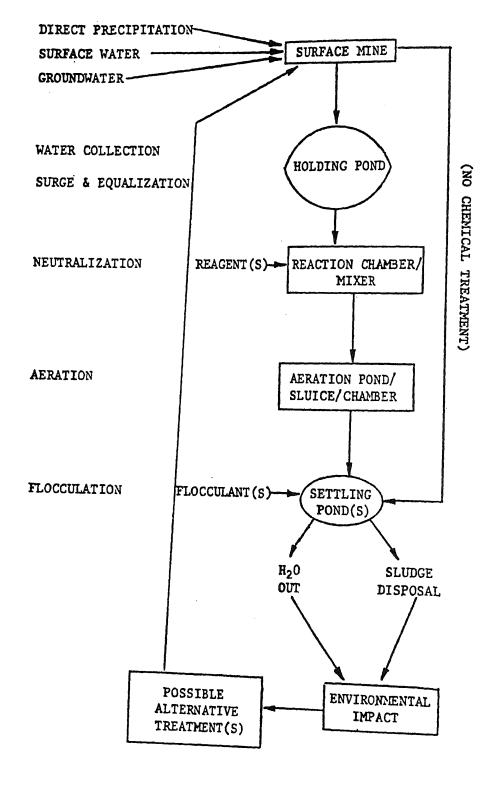


Fig. 2. Subunit Operations: Mine Drainage Geochemistry (Task 2)



data bank brotage and retrieval systems. Input data include enci analyses of surface water, coal, and overburden, as well as background information on sites and methods of sampling and analysis. TASK 4 - EFFLUENT LIMITATIONS GUIDELINES

examined in relation to EPA's recently established effluent limitations guidelines and new source performance standards for the coal mining por source category. These standards and effluent limitations have been in porated into the Office of Surface Mining Reclamation and Enforcement's proposed rules for a permanent regulatory program. The applicability of guidelines and standards on a national scale versus state or regional s will be analyzed. The data from this program will be used to assess the validity of the guidelines in general and in relation to current and fu

will be developed. Figure 4 shows the operations which will be utilize

chemical data from the various sites with a discussion of generic envir mental control problems, the pollution control technology involved, and the control technology effectiveness. Included in this final report w be recommendations for environmentally effective control technology for

RESULTS

Two examples of program output -- control technology efficiency

The mine effluent analytical data gathered under Task 2 are being

Recommendations for modifying or implementing the guidelin

Argonne National Laboratory will write a summary report integrat

TASK 5 - SUMMARY REPORT

in Task 4.

of new mine openings, and alternate control technologies for existing a expanding mines. Recommendations will also be made for research on adcontrol technologies based on criteria and needs determined by this pro

treatment costs -- are described in this report:

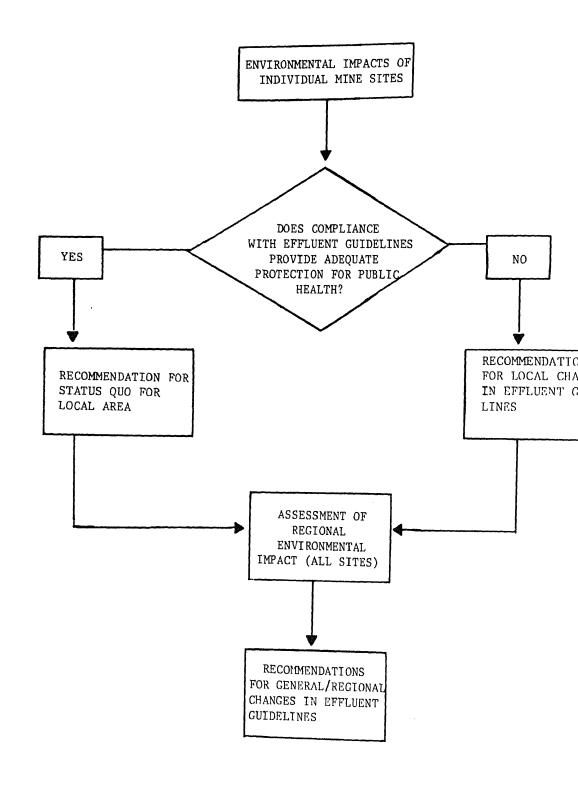
CONTROL TECHNOLOGY EFFICIENCY

Mine PA-1

Two mines in Pennsylvania, PA-1 and PA-3, serve as examples of adequate and inadequate treatment. At mine PA-1, water from an active is pumped through a six-inch flexible vinyl hose for several hundred y to a flash mixer powered by the water velocity from the pump. The mix

is housed in a small wooden shed. Approximately 50 pounds of hydrated lime is manually added to the mixer every two hours. The mixer efflue flows through a wooden sluice box into the first of three settling pon-

Most of the sludge and sediment is retained in the first pond; retenti time for this pond is estimated to be approximately nine hours.



allowable maximum standards in three out of twenty-six sampling visits; iron values were in violation twice during the sampling period. Following treatment, data from the first settling pond outflow (F indicate compliance (maximum allowable) was attained for the mean of all four parameters, although occasionally levels of suspended solids (three out of 23 visits) and manganese (three out of 22 visits) were in violati of the standards.

mentalism beautiful for suspended sortus and mangamese, thatcaes

Data from the second settling pond outflow (C) show a lesser inci

treatment was necessary. Values for pit water pH were in violation of t

of violating the maximum allowable standards. In general, the effluent discharged from this site met the maximu allowable effluent limitations. The lime treatment was adequate and There were occasions when pH, manganese, and suspended solid levels were not in compliance, a situation reflecting inadequate process

controls since the operation is manually operated and controlled.

Mine PA-3

and manganese only 10% of the time.

Water treatment at mine PA-3 consists of collecting pit water in sump; adding an alkali reagent occasionally, but not necessarily regular then pumping the effluent into the first of three settling ponds. The a

coal fines. A secondary treatment, only occasionally used, consisted of perforated bucket filled with soda ash briquettes or hydrated lime below outflow of the first settling pond. The values listed in Table 3 show the pit water (mean values for suspended solids, manganese, and iron and the range of values for pH) in

soda ash (Na₂CO₃), is mixed by hand with pumped pit water in a 55-gallor drum that is perforated in its lower portion and base to allow the disso reagent to flow back into the sump. The water pumped into the settling had minimal retention time as the ponds were nearly filled with solids,

tion of the maximum allowable standards for each of the four parameters. ing treatment some improvement was noted in all four parameters, but the

values (B) still show the mine is not in compliance. Only once during entire range of sampling dates was the pH raised to an acceptable level. but on this date the suspended solids reached 1800 mg/L indicating only partial treatment, poor settling sludge characteristics, and probably inadequate retention time. Iron levels in the first pond were in compl: on less than half of the sampling dates, suspended solids 60% of the time

Effluent from the final settling pond outflow (C) was in complian only for mean values for suspended solids; although minimal improvement was noted, mean values for pH, iron, and manganese were still in violation

of the guidelines. For the final effluent leaving the mining site, vio of standards for suspended solids occurred on 20% of the sampling dates Effluent

pH^a	Within range of 6.0 - 9.0	
Total suspended solids ^b	70.0	35.0
Iron, total	7.0	3.5

Maximum

Allowable

Average of daily values for 30 consecutive

discharge days

2.0 Manganese, total^c 4.0

Where the application of neutralization and sedimentation treatment technology results in inability to comply with the manganese limitations set forth, the regulatory authority may allow the pH level in the discharge to exceed to a small extent the upper limit of 9.0 in order that the manganese

limitations will be achieved. bLimitations given are for eastern and midwestern states.

Western states are treated on a case-by-case basis, but levels must not be greater than 45 mg/L (maximum allowable) and 30 mg/L (average of daily values for 30 consecutive discharge days) based on a representative sampling.

 $^{^{\}mathtt{c}}$ The manganese limitations shall not apply to untreated discharge which are alkaline as defined by the EPA (40 CFR 434).

Effluent	Standard	M	ean	Min.	Max.
рН	6 - 9			3.6 6.3 4.2	7.3 8.8 8.3
Total suspended solids	70 mg/L	A. B. C.	162.4 39.3 14.6	14.0 4.0 0.0	1380.0 203.0 124.0
Total iron	7.0 mg/L	A. B. C.	4.1 1.0 0.5	0.0 0.0 0.0	14.0 3.8 2.8
Total manganese	4.0 mg/L	A. B. C.	5.3 2.4 1.7	1.2 0.5 0.2	29 4 3
B. First p samples C. Final p	er, 26 samples ond outflow, 2 for manganes ond outflow, 2	23 sam e). 26 sam	ples.		,
B. First p samples C. Final p Table 3.	ond outflow, a for manganese ond outflow, a Mine PA-3 (Un	23 sam e). 26 sam nits i	ples. n mg/L e	except pH	
B. First p samples C. Final p	ond outflow, 2 for manganess ond outflow, 2	23 sam e). 26 sam nits i	ples.		Max. 5. 8.
B. First p samples C. Final p Table 3.	ond outflow, a for manganese ond outflow, a Mine PA-3 (Un	23 sam e). 26 sam nits i	ples. n mg/L e	Min. 3.2 3.5	Max. 5. 8. 6. 2600. 43350.
B. First p samples C. Final p Table 3. Effluent pH Total suspended	ond outflow, a for manganese ond outflow, a Mine PA-3 (Un	23 sam e). 26 sam nits i M	n mg/L e ean 185.6 2544.6	Min. 3.2 3.5 2.9 0.7 5.0	

```
In contrast to mine PA-1, effluent discharged from mine PA-3 ra
met the effluent guidelines. The soda ash treatment was erratic, tota
uncontrolled, and inadequate. The sedimentation ponds were nearly fil
with solids and channels developed which allowed the water to pass rap
through the ponds, resulting in negligible retention time for floccula
and settling of solids. Often the suspended solids concentration incre
between the pit water and the final settling pond.
TREATMENT COST FOR MINE PA-1
       Since mine PA-1 is conscientiously attempting to comply with the
effluent limitations guidelines, an examination of its most recent trea
cost data gives an indication of the level of costs that the industry
in maintaining compliance.
       Mine PA-1's operation ultimately will affect 100 acres, 95 of wh
contain coal. The average coal thickness is 3'1" and, at the standard
of 1800 tons/acre ft of coal, each acre contains approximately 5600 tor
of coal. At a recovery rate of 90% for surface mined coal, this mine w
produce 478,800 tons of coal (95 acres x 5600 tons/acre x 0.9 [recovery
478,800 tons).
       In order to control the sediment related to the mining, storage
and diversion ditches need to be constructed and, after mining ceases,
and reclaimed. The sediment collected in these ponds during the mining
operation must also be removed and handled in a manner consistent with
environmental standards. The following costs and assumptions were base
on discussions with on-site company personnel. These costs are life-of
mine costs and are related to the total tonnage the mine is expected to
produce.
       Sediment Control
       1. Pond Construction
           Sediment storage: 0.2 acre ft/acre of disturbance x 100 acr
                              disturbed = 20 acre ft.
           Storm water storage (10 yr - 24 hour storm): 4" rainfall x 0
                              (runoff coefficient) x 100 = 17 acre ft.
           Total capacity needed = 37 acre ft.
          Plan: 3 ponds, 12-15 acre ft. each.
          Cost per pond:
                    Earthwork and seeding
                                                  $ 8,000
                    Discharge pipe
                                                  $ 1 500
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Sediment removal: Assume 10 acre ft (16,100 cu yd of sedimen
                             Removal and disposal @ $2.50 \text{ cu yd} = $40.2
          Pond removal = 1/2 of construction cost = $20,500.
      3.
          Diversion Ditches
          9000 ft @ $2.50/ft = $22,500.
          Removal = 1/2 of construction cost = $11,250.
          Total = $33,750.
          Note: 6500 ft of ditch built under old law specifications
                 exists. Estimated cost of that ditch, 6500 ft x
                  $1.50/ft = $9.750. New cost under new law = $24,000.
      Summary of Sediment Control Costs
                                          $ 40,500
          Pond construction
                                         $ 60,750
           Sediment and pond removal
                                         $ 24,000
          Diversion ditches
           Total cost
                                         $125,250
           Cost/ton - $125,250/478,800 = $0.26/ton.
      The water treatment costs were provided by the company following
its investigation of compliance costs for a recent six-month period in I
to meet the new effluent limitations. The mine has complied with most
effluent discharge criteria except for periodic violations of the mangan
limitation. Production was 65,000 tons for the six-month period.
      Water Treatment Cost - Six-Month Period
       Equipment and Power
                                                            $ 3,900
                                           $650/month
          Pumps, hoses, and misc.
                                           $350/month
                                                            $ 2,100
          Electric and fuel
                                           $ 55/ton
                                                            $ 5,500
       Lime (100 tons)
       Ponds
                                                            $ 1,800 eac
          3 @ 1.8 acre ft each pond
                                                            $ 1,200 eac
          Earthwork
                                                            $ 3,000 eac
```

Sediment and Pond Removal

Equipment and Power

Equipment and Labor

Engineering and Management

Cost/ton = \$166,650/65,000 =

Lime

Ponds

Total

for full compliance.

Engineering and Management

a	b	0	r

101

ab	or	

15% of equipment and 1 Summary of Water Treatment Cos

sts	(Si

Total sediment control and water treatment cost = \$2.82/ton.

our other eastern sites because the affected area of the mine has rathe shallow slopes. As the slope angle increases, our preliminary findings indicate a corresponding rapid increase in sediment control costs, with final costs often exceeding \$7/ton. The costs presented for mine PA-1 still do not represent costs for total compliance, as the manganese sta is often violated. The company estimated an additional \$0.65-\$0.75/tor

The total cost of \$2.82/ton is relatively low compared to costs

CONCLUSIONS ON CONTROL TECHNOLOGY EFFECTIVENESS

The major conclusion drawn from this survey of control technolog

1. At the present time, mine drainage control and treatment at surface coal mines may not reflect conscientious planning

whole, control technology (including reagent application) may be haphazard and periodically inefficient. However,

all, portable application systems for neutralization reagent Because effluent discharge points at surface coal mines do not remain constant over long periods of time and because discharges are generally small (< 5 gpm) and variable, it is

2. Surface mine operators favor small, efficient, and above

at sites PA-1 and PA-3 and at other surface mines is that the ECT "stat of-the-art" is generally at a very low level. Related conclusions incl

and engineering design work by mine operators.

there are some notable exceptions.

(x Months)

\$21,700

\$ 21,700

\$ 6,000 5,500

\$ 9,000

\$124,450

\$166,650 \$2.56/ton 3. When choosing a reagent to neutralize mine drainage, reagent cost per unit quantity is less of a deciding factor to surface coal mine operators than ease of reagent application and handling. Thus, small caustic soda (NaOH) and soda ash (Na₂CO₃) treatment systems are common, even though reagent costs (based on treating

cost of hydrated lime or limestone treatment.

and after mining, a long and costly process.

water of equivalent acidity) may be several times the

- 4. There needs to be more pre-mining planning by surface mine operators to develop mining methodologies which minimize pyrite oxidation and hydration. Some additional investment in exploration plus a prudent choice of a mine plan, drainage plan, and reclamation plan may minimize the generation of poor quality effluents. Mine operators may thus realize economic benefits from minimal initial investments which prevent the generation of poor quality effluents, as opposed to the operators' maintaining treatment facilities during
- 5. Costs for compliance with EPA/OSM effluent limitations can range from \$3-\$7/ton. The higher costs are associated with steeply-sloped terrain.

OF COAL DURING TRANSPORT AND STORMED

R. V. Kromrey

R. S. Scheffee R. S. Valentine

Atlantic Research Corporation

Alexandria, Virginia
1. INTRODUCTION

R. Naismith

I. INTRODUCTE

Coal from mines is transported to its ultimate destination by rai barge or pipeline. Once it arrives at its consumption point or a proc facility, it is moved over short distances by rubber-tired loaders, co or rail shuttle cars. During the transportation process, the coal is

or rail shuttle cars. During the transportation process, the coar is exposed to the elements. This leads to dust emissions and losses thro effects. Moisture absorption and oxidation also can occur, causing de tion of the coal and loss in fuel value (ERDA, 1976).

Once at the destination, the coal is either used or stored. Most maintain stockpiles comprising a 90-day supply at their normal use rat is done primarily to provide a reserve in the event of temporary loss ply. This stockpile may stand for a year or more before it is necessary.

ply. This stockpile may stand for a year or more before it is necessa use it.

In the stockpile, the coal is subject to weathering and oxidation dust emissions from stockpiles are common. Absorbed moisture from rain causes leachate formation and may decrease the fuel value of the coal

8% depending upon initial moisture level and coal rank. Wind and rain results in coal migration and exposes new coal surface to weather. Mo can also freeze solid in cold weather making normal handling impossible dation may reduce the heating value up to 5% over a one-year storage per (ERDA, 1976). In addition, internal oxidation can lead to spontaneous tion in low rank fuels (ERDA, 1975; Paulson, et al., 1975).

handling characteristics, but can also be shown to provide dollar saving substantially greater than the costs of application.

2. TECHNICAL APPROACH

This work presented here addresses the use of protective coatings coal to resolve the environmental problems associated with transport as storage. These coatings not only reduce environmental pollution and in

The overall objective of this work was to demonstrate the feasibil economical coal coating systems. To accomplish this, the following factories considered:

- Identification of suitable materials for coal coatings
- Development of formulations which are capable of reducing the adverse environmental effects of weathering of coal storage

Cost/benefit analysis

mental development of coal coatings. The factors considered are listed b Evaluation of candidate filler-binder materials Review of current coal protection techniques

Application considerations User motivation

The first task was intended to provide information to guide the expe

Filler-Binder Materials Evaluation

A list of materials was generated which could be considered as candi for inclusion in coal coating formulations. The candidate materials were screened to establish their characteristics with respect to:

- Cost Availability
- Fuel value
- Physical properties
 - Environmental pollution potential

The filler materials considered included coal, paper, sawdust, bagasse, r hulls, cottonseed hulls, and fly ash. Binder materials considered fall in two categories. The first included the materials useful for the hot-melt

of coating such as waxes and plastics. The second type of binder materia the various latex emulsions. This type of material was considered for use filled latex coatings.

Pulverized coal and fly ash emerged as the best filler candidates. of these materials are available at coal user sites in sufficient quantit They are both available at little or no cost, taking into account the crefor fuel value of coal. Neither of these materials would cause additional

environmental problems upon combustion, as both are normally present in co combustion systems. The other filler material candidates were either too costly, limited in availability or presented potential environmental prob The best binder materials identified were slack wax, polyethylene, atacti-

polypropylene for the hot-melt composition, and polyvinyl acetate copolym

Current Coal Protection Techniques

current protection methods is provided below.

for the filled latex formulations.

The most common current means of protecting coal is to carefully bui and compact the stockpile, then monitor it for hot spots. At this time,

estimated that less than 5% of the users of coal provide additional prote in the form of coatings. Coal is shipped by rail car in as-dumped condit It is estimated that 5-10% of the shippers use latex crusting compounds to prevent wind loss and dust emissions in transit. A discussion of these

Ctaskaila Formation

required. Stockpiles must be properly constructed; otherwise, the risk of \mathbf{s}_1 neous combustion is high. Coal stores have been known to ignite sponta within six days after pile formation (Wilson, 1975). A typical method

constructing a coal stockpile is given below. The coal is dumped from the rail cars either by bottom hopper 1. invention. The coal falls onto a conveyor and passes through a mill when

ground to <2-inch size pieces. The coal is transported to the stockpile areas either by conv 3. by rubber-tired vehicle. A bulldozer spreads the coal and compacts it. Typical piles 4.

the form of a truncated cone, 100-200 feet wide at the base a 25-50 feet high. The length of the pile may be up to thousar feet.

Coal as dumped has a bulk density of about 50 lb/ft3. After compaction bulk density is about 65 lb/ft³ (Paulson, et al., 1975). The stockpiling technique varies with coal source and rank. Higher coal may be formed into larger piles of greater height and stored longe low rank coals (ERDA, 1975). East coast coals may be stored longer tha

coast coals as they are less reactive. The finer the coal, the more re

it is as a result of greater surface area. Small coal stockpiles may be stored as dumped for short periods. piles should not exceed 15 feet in height (Wilson, 1975). Longer term s of uncompacted coal is risky in terms of spontaneous combustion danger.

Uncompacted coal piles should be used within a few days of dumping.

2.

Stockpile Protection

Stockpiles are formed solely by the action of a bulldozer in shapi: compacting the pile. Thermal probes are sometimes buried in the coal t

tor pile temperatures. The probes set off an alarm if the pile tempera reaches 130-140°F (54-60°C).

Dust emissions from coal stockpiles are a problem of increasing con Some users reduce dust formation by washing the coal before piling and porting it wet. Other users wet the pile after formation or spray it w to reduce dust emissions.

Leachate formation is also a serious problem except in the case of high grade coal. Water runoff from the pile is collected in a trough as the pile. It is then sent to a holding tank or pond where it is treated fore discharge to the environment. The treatment generally consists of ducing a flocculant or precipitating agent, then allowing the cold by

Latex Crusting Compounds

The only protective coating of significance in current use is the later crusting compound. This material is essentially a paint base, and it is duced by paint manufacturers. Numerous small firms purchase this material

will lose only 1-2% per year of its energy value due to oxidation.

improper storage was found to result in losses of 3-5% per year.

in the first year of storage. Leonard (1968) found that properly stored

onto the material to be protected using any equipment capable of spraying

Howev

duced by paint manufacturers. Numerous small firms purchase this material resell it as a protective coating for coal or as a surface stabilizer for earth, sand or other materials stored in stockpiles. The latex compounds normally applied after dilution by a factor of 3/1 to 20/1. They are spra

Formulation and Evaluation of Coatings

During this work, 119 hot-melt formula

During this work, 119 hot-melt formulations and 39 latex mixes were duced and evaluated. The types of tests conducted were as follows:

Visual observation Viscosity
cracking tendency Density
surface texture Thermal expansion

adhesion to substrate Water permeability
Compressive strength Rheology
Tensile strength Grindability

Not all tests were run on all formulations. Some tests, such as tensile

compressive strength, were run on a limited number of specimens to estable the order of magnitude of the results. No means of converting strength defined a useful parameter for characterizing the utility of coatings was idefied. Thus, the data are of interest primarily as a means of estimating cracking potential.

Other tests, such as water permeability, effects of thermal cycling an efficient of thermal expansion relate directly to the quality of the coat Tables I and II summarize the results of these tests on formulations that

near the optimum compositions for both the hot-melt and filled latex coat

Test Panels

Those formulations which appeared to best meet the above criteria we

cast onto frames, 12" x 12", with about 3-4" of coal as a substrate. The frames were constructed with wooden pegs spaced at 3/4" intervals around periphery. The pegs served to restrain the coating from shrinkage to enh crack formation and present a more realistic test than would an unrestrait coating. The coating was applied in thicknesses ranging from 1/8" to 1/2

Figure 1 shows two views of a test frame with a hot-melt coating in place Figure 2 shows a cross-section view of the coating on a coal bed.

The test frames were subjected to a "rainfall" test. In this test.

STRAIN IN Physical Properties of Hot-Melt Formulations STRENGTH, (70°F) COMPRESSIVE Tangent TENSILE PROPERTIES (-30°F) Ś At Rupture Stress (PSI) Table I. VISCOSITY Avg. KP RPM 2.5 COMPOSITION

)	Avg 25	
302	248 278 249	

Avg 258	Avg 173	
278 249	148 179 192	
		106,000 18,200
		0.4
		210
		4
		7
		œ
Coal SW PE	Coal SW PE	Coal

85.0% 12.0% 3.0%

7

85.0% 12.0% 3.0%

디

PE

85.0% 12.0% 3.0%

4-

NO.

	1.8 2.1 2.1
	Avg 258
1))	248 278 249

رب ق ا	
COMPRESSION At Failure (%)	1.9
at Failure (PSI)	333 392 Avg 342
Modulus (PSI)	
strain (%)	

Coal MS

DENSIŢY GM/cm (70°F)

۰ ۲

1:1

2.2 1.9 2.3

1.08

84,800 68,200 83,600

0.6

222 233 241

Coal

SWPP

80.0% 15.2% 2.4%

Polypropylene Polyethylene

Slack Wax

SW PP PE

77.5% 14.9% 3.8% 3.8%

	E 1 1		4	# 4	. T	, ,	4	
	Table 11		aracteri	Stics of HO	characteristics of hot-meit and filled Latex Compositions	гатех сощ	positions	
RENCE NUMBERS	LEAK RATE, 70°F +160		% OF SPRAY		36" CTE STRIP Shrinkage Reheat Shrinkage	AVERAGE	AVERAGE RESTRAINED CTE ENDS GAP	GRINDABILITY
80.0% Coal 13.4% SW 3.3% PE 3.3% PP	3.3	8.1	11.0	0.335"	I	7.6×10 ⁻⁵	ı	Fair

Fair

ı

 6.6×10^{-5}

ı

0.305"

8.0

5.2

1.4

77.5% Coal 14.9% SW 3.8% PE 3.8% PP Fair

0.118"

 6.2×10^{-5}

0.278"

0.285"

78.0

20.0

14.0

80.0% Coal 15.2% SW 2.4% PE 2.4% PP

2, 5-30-1

7.7

acetate

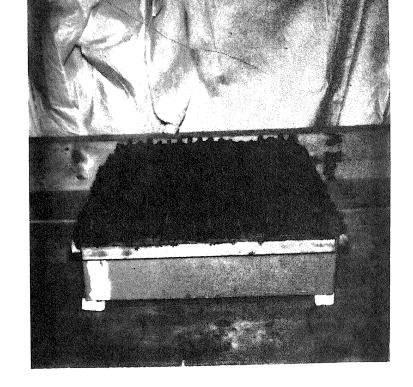
50.0% Coal 23.0% Vinyl

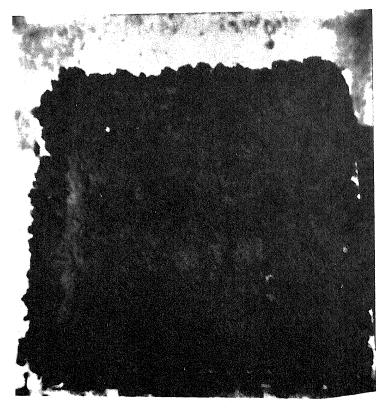
copolymer 27.0% Water

Polyethylene Polypropylene

Slack Wax

Good







to-failure of a coating material, cracking will result. Similarly, if thermal expansion upon heating exceeds the compressive strain-to-failure coating will shatter.

The coatings listed exhibited Coefficients of Thermal Expansion (C ranging from 6 x 10⁻⁵ to 14 x 10⁻⁵ in/in°F. Thus, for a 100°F temperat change, the degree of expansion or contraction would be about 0.6% to 1 The tensile strain to failure was measured to be about 0.5%. Thus, mos ings would be expected to crack upon cooling by 100°F or more. Heating not appear to be a problem. Compressive strain-to-failure was measured about 2%, and none of the coatings tested expanded that much.

Thermal expansion or contraction is an important characteristic of melt coatings. If the degree of contraction upon cooling exceeds the s

The CTE is not the only factor in cracking of the hot-melt coatings materials were generally cast at 200-250°F. In general, the coatings refluid until they cooled to below 200°F. They then start to shrink, if strained. Total shrinkage upon cooling to 70°F ranged from 0.6% to 1.75 cooling behavior was a function of the composition, however. The CTE cofor typical compositions are shown in Figures 3 and 4. Formulations with

values similar to that shown in Figure 4 would probably be satisfactory

Latex Formulation Results

A total of 39 latex formulations were prepared and evaluated during

work. Included in this number were four tests of commercially available crusting compounds for comparison purposes. The remainder of the formulaere filled latexes, in which pulverized coal was used as an extender to

stockpile applications.

Some of the latexes tested were not compatible with coal. In the proof coal, they coagulated or solidified rapidly. Daratak SP-1065, Everfland DLR-H resins yielded satisfactory coating films. All others tested

incompatible with the coal.

The probable reason for the observed incompatibility is de-emulsifi of the resin by chemical reaction with ionic components of the coal. An possibility is instability resulting from pH change because of acidic su

prove the waterproofing character of the latexes.

stances in the coal.

Filled latex coatings made with polyvinyl acctate was

Filled latex coatings made with polyvinyl acetate resins were appli 1-ft x 1-ft panels similar to those previously described for the hot-mel ings. All of the coatings were leakers in the "rainfall" test. The bes these coatings was an Everflex GT mix with 50% coal, which exhibited onl

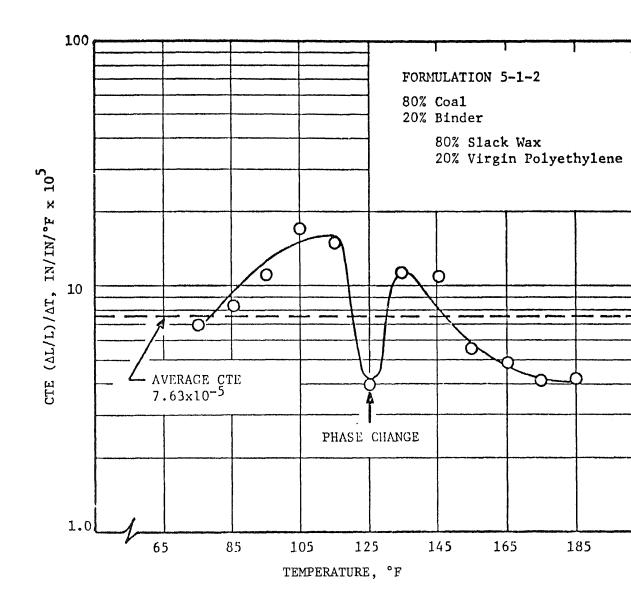


Figure 3. Coefficient of Thermal Expansion Curve for Formulation 5-1-2

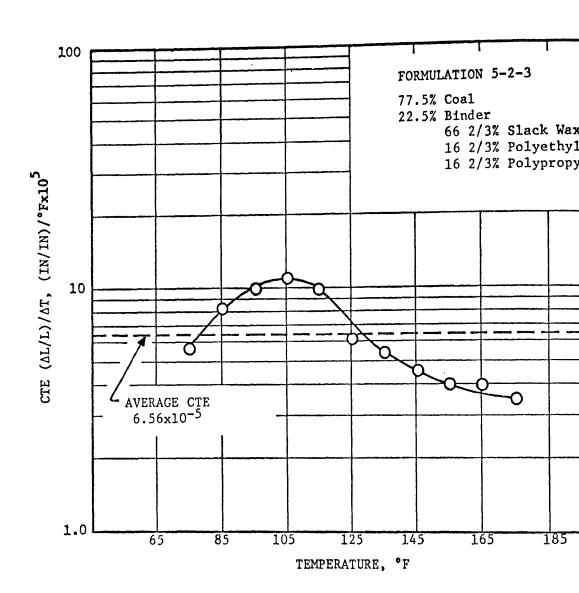


Figure 4. Coefficient of Thermal Expansion Curve for Formulation 5

coating did form a conesive film on the surface, however. Less than 8% of the "rainfall" water abdered to the surface or passed through the coating even after exposure to a temperature range of -30°F to +160°F. In the ed nomic analysis, presented later in this paper, filled latex coatings on b normal and specially prepared surfaces are considered for comparison purp Tests on commercial latex crusting compounds showed that they do not vide a significant degree of waterproofing to coal. The minimum leak rat noted was 78%. One commercial product was tested at the recommended cond tration and again at 5 times the recommended amount. The leakage rate wa similar in both cases. The unfilled latexes cannot be considered as a sa

factory waterproofing agent for coal stores even when applied at substant higher levels than recommended by the manufacturers for dust control and

melt materials. The principal objective was to assure that the materials could be pumped without problems due to viscous effects or vapor lock. I tial experiments showed that compositions containing 80% coal were easily

Application Techniques

face stabilization.

Application experiments were conducted to assess characteristics of

transported through a one-inch diameter tube. Flow was initiated with le than 2 psig pressure differential. A system capable of applying hot-melt materials comprises the follow

f)

g)

h)

i)

Slurry pump (heated)

Steam boiler

Dispensing system

Service lines (heated)

elements:

a)

b)

c) Coal preheater d) .Metering system

Crusher/grinder

e) Mixing vessel (heated)

Polymer melt vessel

A schematic of the system is shown in Figure 5. As shown, a mixing vessel is included in the current subscale apparatus. This mixer is used

system would be more desirable. Hot flow application resulted in an excellent layer of coating on an

a batch heater and dispenser. For larger-scale applications, a continuou

clined 4 x 8 foot panel. The material thickness varied from 1/8 to 1/4 i thick. Figure 6 shows a technician in the process of coating a 4x8 foot

3. ECONOMIC ANALYSIS

The following section is an evaluation of the costs and benefits whi would accrue from the use of protective coatings for coal. Uses of latex crusting compounds, filled latex coating and hot-melt coatings are consider

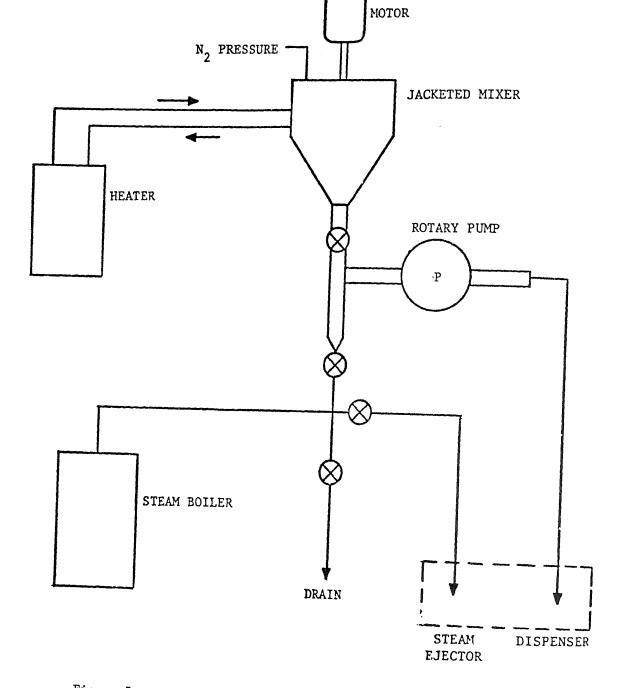


Figure 5. Schematic Diagram: Coal Cover Application System



Figure 6. Application of Hot-Melt Coatings

Dump coal from cars
Grind to <2 inches
Transport to pile
Unload on pile
Form and compact pi
1

Latex Crust

3-10/1

Mix with water,

pile

1.

4.

Filled Latex

Spray apply 7-31 gal/

stockpile. A 250,000 ton stockpile was used as a basis for comparison.

preparation*

Grind coal for surface

Grind coal for 1. coating mix Prepare wax/pla binder

Hot Melt

Current practice, unprotected pil

Spray apply 4-11 gal/500 ft²

2. Grind coal for coating mix Mix coal, water, latex 3.

500 ft²

3. Heat and mix components Spray apply 20-

ga1/500 ft2

* optional

2.

Summary of Stockpile and Rail Car Protection Costs

Table IV shows a summary of the costs of building and protecting a co

Table V is a summary of the costs of various techniques for protecting coa in rail cars.

Table IV. Summary of Stockpile Protection Costs

Basis:	Basis: 250,000 ton stoc		
Treatment	Time RequiredDays	Total	
Build and Compact Stockpile	50	55,	
Monitor Stockpile for 1 year	365	22,	
Latex Crusting Compound, 1 gal/200 ft ²	3.5	8,4	
Filled Latex on Surface Fines, .025"	13.3	19,	
Filled Latex on Surface Fines, .050"	26.6	25,9	

Filled Latex on Surface Fines, .100" Filled Latex on Normal Surface, 1/8"

Hot-melt on Normal Surface, 1/8"

Hot-melt on Normal Surface, 1/4"

53.2

11.7

11.17

23.4

al Cost Cost/ \$ 5,000 0.2 2,750

33,506

12,788

25,576

0.0 3,400 0.0 ,500

0.0 ,908 42,000

0.1

0.1 0.1 0.0

0.10

Total Cost

\$

700

3,844

Cost/Ton

\$

0.07

0.38

Filled Latex on as Dumped Surface, 1/8"	4,320	0.43
Holt-melt on as Dumped Surface, 1/8"	1,355	0.14
Cost/Benefit Analysis - Stockpile Appli	cations	
This section illustrates the benefits t	o be derived from co	al protec
and the estimated return on investment. Thi		
tion of a 250,000 ton stockpile for a period	of one year. The v	alue of t
coal is assumed to be \$20 per ton.		
The cost factors used in determining tr	eatment costs are li	sted belo
	Cost, \$/Ton	
Build and compact pile	0.08	
Apply latex crusting compound	0.034	
Apply filled latex coating, 0.025"	0.087	
Apply hot-melt coating, 1/8"	0.051	
The benefit factors used in determining	the return on cost	of applyi
particular coatings are:		
Reduce or eliminate dust emissions	•	

Minimize freezing of coal into large agglomerates. Prevent increase in moisture content (grinder operation). Prevent stockpile migration.

Reduce or eliminate oxidative energy loss.

Reduce or eliminate leachate formation.

Reduce or eliminate spontaneous ignition.

Prevent wind or rain erosion.

Reduce need for snow removal.

Reduce monitoring costs.

Treatment

Latex Crusting Compound, 1 gal/500 ft²

Filled Latex on Surface Fines, .050"

Reduce fire prevention and extinguishment requirements.

Maintain or reduce moisture content (fuel value effect).

The basis for determining the dollar value or equivalent for these benef factors is described in Kromrey, et al., (1978). The results are summari From this summary, the highest return per unit cost occurs by use the hot-melt formulation, i.e., return of benefits valued at \$1.90 per to a cost of 13.1¢ per ton.

0.158 1.04 Filled Latex Coating* 1.04 0.131 Hot-melt Coating* * includes compaction Cost/Benefit Analysis - Rail Car Applications

T.00

1.90

Total Benef:

\$/ton

0.74

This section illustrates the benefits to be derived for protection coal in rail cars and the estimated return on investment. The results based upon protection of a unit of 100 cars containing 100 tons each of

The value of the coal is assumed to be \$20 per ton. The benefit factor sidered are listed below:

Treatment

Latex Crust

Reduce or eliminate dust emission.

Reduce wind losses.

Prevent moisture increase (fuel value effect). Prevent moisture increase (grinder operation).

Prevent freezing of coal into large agglomerates. Reduce or eliminate spontaneous combustion.

Again, the basis used to convert these factors into an equivalent dollar value is described in Kromrey, et al. (1978). The results are summarize below. This summary indicates the benefit return per unit cost to be had for the latex crusting compounds with \$.74 per ton in benefit value resu

from costs of \$.07 per ton. For rail car applications, the latex crust pears to be most cost-effective. Treatment Costs, Direct \$ Savings, Value, Equiva

\$/ton

0.07

Filled Latex Coating	0.38	0.61	0.81
Hot-melt Coating	0.14	0.61	1.01
	4. (CONCLUSIONS	

Based upon the results of this technical effort, the following cond sions are presented:

1. Commercially available latex resins used as coal crusting comp can prevent dust loss and wind erosion, but do not waterproof coal surface.

\$/ton

0.54

Hot-melt formulations consisting of about 77.5% coal, 15% slad 2. wax, 3.75% polyethylene and 3.75% polypropylene are capable of sealing a coal surface against water penetration.

Hot-melt coatings appear to be most cost effective for application 4. to coal stockpiles. Latex crusting compounds appear to be the most cost effective mean 5. of protecting coal in rail cars.

water penetration provided the surface is coated with fines of

6. The anticipated return in dollars and intangible benefits by use of the coal protection methods described herein is in the range of 10-15 times the cost of such protection.

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ABSTRACT

Enhanced oil-recovery processes are still developing.

T

transition from pilot testing to full-scale field application depends upon the success of field research that may improve to economy of enhanced oil-recovery processes. Underlying all development and expansion activities associated with oil production is the constant need to protect the environment from polition. Unanswered questions regarding the environmental consequences of enhanced oil-recovery activities should be addressed during the period of pilot field testing.

Oil displacement by injection of brines (the waterflood process) entails the surface processing of large quantities of saline waters creating the potential for pollution of surface waters and shallow freshwater aquifers. Improved waterflooding techniques involve the introduction of surface active agents (detergents), caustics, and organic polymer compounds (particularly polyacrylamide), thus increasing the potential for pollution. It is increased further by the micellar-polymer process since the micellar solution is a mixture of surfactant, oil, water and a cosurfactant (usually an alcohol).

Enhancement of oil production by thermal methods adds and dimension to the environmental hazards through air pollution f steam generators and the produced fluids.

Other field operations, such as drilling and renovation of wells, create local environmental hazards, but these are become regional concerns as the search for new oil and the reactivation of old oilfields accelerates. This paper presents the potential pollution hazards of the enhanced oil-recovery processes and the environmental surveillance program being instituted by DOE.

INTRODUCTION

We are safe in predicting that the future will bring with it a greater population density. To maintain our standard of living, engineering technology will have more stringent demand

making life comfortable and healthy. However, in filling consumer needs, engineers cannot ignore the ecological considerations of every technological process. Governmental controls, economic considerations, and diminishing resources have forced complete re-evaluation of waste effluents from all industries. Waste must be negligible for the sake of the economy as well a providing safety within the environment in which we live.

Enhanced oil-recovery processes are still developing. The transition from pilot testing to full scale field application

production is the constant need for protecting the environment from pollution. Unanswered questions regarding the environment consequences of enhanced oil-recovery (EOR) activities should addressed during the period of pilot field testing, now in progress. Environmental data can be obtained from pilot projects that discharges can be correlated over time with reservoir characteristics and process variables for use in planning field wide commercial implementation of any process.

Potential adverse environmental concerns are enhanced by injection of large quantities of chemicals to displace oil in producing wells. New chemical processes for oil recovery requirements.

surface processing of large quantities of saline waters as we as chemical mixtures. The large volumes of fluids create a

depends on the economic success of field research. Underlying all development and expansion activities associated with oil

potential for pollution of surface waters and shallow freshwate aquifers. When the oilfield is finally abandoned large quants of chemicals used for oil displacement will be left in the uncommended reservoir, creating a potential for long-term environmental hazards.

The United States Congress and State Legislatures have enacted laws intended to protect our environment from pollutions and the state of the

enacted laws intended to protect our environment from pollutic due to human endeavors. Several of these laws have a direct bearing on enhanced oil recovery, the most significant of which are the Clean Air, Federal Water Pollution Control, and Safe Drinking Water Acts.

recovery is the best way to avert adverse environmental effects. The Department of Energy has initiated several research project to examine the biological and chemical degradation of EOR chemicals, the effects of injected chemicals on geologic strata, toxicity of chemicals, water availability, and the socio-econd aspects of enhanced oil recovery. This paper is a general over

view of the environmental concerns of the enhanced oil-recover

Research with chemicals intended for use in enhanced oil

specific aspects of developing technology. Concern for the environment means that we do not wish to produce any kind of adverse effect on the air, water or soil our activities. Therefore, the processes being used today fo production of oil, as well as the new enhanced oil-recovery methods being field tested, are discussed from the viewpoint their potential for adversely affecting air, water and soil. is important to emphasize that the current EOR field activiti of DOE are nothing more than research experiments. The costshared field testing program with industry is designed to eva the utility, demonstrate the feasibility, and improve the tech niques of the best technology presently available for product of oil remaining locked in the ground after secondary recover In pilot experiments, the environmental impacts are confined widely scattered, isolated local sites. We tend to lose sigh this in considering the national concern over possible adverse

production in the United States. A Programatic Environmental Impact Statement on the enhanced oil-recovery activities of t Department of Energy, which is now being prepared, will addre

EOR PROCESSES AND ENVIRONMENTAL CONCERNS

commercialization can proceed in a timely manner.

Secondary Oil Recovery

Secondary recovery (waterflood process) is conducted by

environmental impacts from any activity. Although this report addresses the environmental aspects of EOR, it is a projection the hypothesis that the demonstration experiments now under wa will prove to be successful and result in large-scale commerc: ization of the EOR processes. By closely examining the pilot studies and looking ahead to commercial implementation, we hope to foresee any adverse impacts of EOR and alleviate them so

injecting treated produced brines into oil-bearing strata to displace the oil to production wells. The brines are treated removal of iron and suspended solids, and, after filtration, a small amount of sodium bisulfite is added to removed entrained Sodium tripolyphosphate is then added to prevent scal formation in the pipes. The addition of the sodium bisulfate tripolyphosphate is a simple process and the concentrations us

are so small that no environmental hazards exist from their us

The accumulation and processing of large volumes of oilfield brines does present serious potential environmental problems, attributed to oil and gas-field brine-injection operations.

On the average, only about 30 percent of the original oil-in-place is produced by primary and secondary recovery methods. The remaining 70 percent of the oil in the ground is the target of tertiary recovery, or enhanced oil recovery, because this resource is estimated to be greater than 300 billion barrels of oil.

Chemical Flood

technology developed for secondary recovery are known as Chemic Flooding (or Improved Waterflooding), and the Micellar-Polymer Process. Chemical Flooding, as the name implies, involves the addition of chemicals to the brine prior to injection. At pres

The two EOR processes that employ, and are based upon, the

three types of chemical compounds are in the forefront of chemical flooding. These are caustics (sodium hydroxide, sodium silicate ammonium hydroxide, etc), detergents (alkyl aryl suflonates), a polymers (polyacrylamide and polysaccharide). A large body of experience has already been accumulated in the use of polymer solutions in oilfields, since more than 100 fields have been treated with polymers of various kinds.

The construction of additional facilities (mixing tanks, storage tanks, pumps, pipes, etc.) are necessary to mix and

storage tanks, pumps, pipes, etc.) are necessary to mix and process the chemical solutions at the field site: however, the additional facilities are not very much different from those us in routine oilfield operations. Large quantities of chemicals will be injected over a long period, but it is not necessary to store large inventories of chemicals at the field site. Hence the potential for environmental damage from storage and operate of the facilities is confined to a small area of the field and is limited to spills or leaks of less than the capacity of a railway car or truck. Precautions against health hazards to personnel using the chemicals in the field must be taken since all of the chemical compounds are severe irritants to mucous membranes.

Chemical compounds produced with the brine and oil are not a cause for concern because only a small fraction of the injection is eventually produced. The amount of chemical injection a chemical flood is designed to be approximately equal to the state of the state o

or below the oil zone when it cannot be used in the brine inj tion program.

storage and processing, (3) Health hazards from the dry chemic and solutions, to personnel operating the field, (4) Leaks from surface storage and treatment ponds for produced brine, (5) Leaks from high-pressure pipes transporting mixed chemicals to the wells, (6) Underground leaks into shallow aquifers from damage or corroded wells, (7) Production into shallow aquifers from improperly plugged abandoned wells (possible when the pressure the oil reservoir is raised due to EOR activities,) (8) Production aquifers above the oil reservoir through an incompetent subove the reservoir (fracture or fault), (9) Subsidence along fault plane caused by increase in reservoir pressure and (10) Subsidence caused by chemical disaggregation of the oil reservoir matrix.

Micellar-Polymer Process

The micellar-polymer EOR process involves four separate

phases of fluid injection beginning with a "preflush" injectio of fresh or low salinity water, necessary to adjust the salini

The major potential environmental problems associated wi

chemical flooding are: (1) Local air pollution by hydrogen sulfide removed from the produced brine during treatment, (2) Spills or leaks of chemical additives during transportation,

and pH of the reservoir. The microemulsion is composed of a hydrocarbon, brine, surfactant, co-surfactants (generally alcoh and electrolytes. The third injected fluid is a polymer solut whose increased viscosity assists in more efficient displaceme of the oil bank and the microemulsion. Brine injection follow the polymer solution as the fourth fluid-injection phase.

Although the micellar-polymer process is considerably more complex, the environmental concerns are the same as those expressor chemical flooding. The application of the micellar-polymer process increases the need for surface equipment and requires additional transportation, storage and a larger variety of chemical compounds. During the injection of chemicals (the second and third phases mentioned above) a large amount of chemicals will be injected in a relatively short time when compared to chemical flooding. Therefore, large inventories of

mental concerns are intensified, but no new ones are added. Health hazards to personnel become greater because larger quantities of chemicals must be processed. Any leaks from surface storage or pollution of shallow aquifers from abandoned

or incompetent wells going undetected for a long period would

result in severe damage to ground or surface streams. However, recognition of intensified environmental concerns should result in more stringent design specifications of equipment and closer surveillance of operations. If abandoned or improperly plugged wells are suspected, monitoring of any fresh water aquifers alo the hydraulic gradient during the chemical injection phases wil be necessary. In field tests of chemical flooding and micellar-polymer processes conducted so far, low-salinity water is used at various

stages (preflush, surfactant solutions, polymer solutions, etc. However, the trend is to design systems less sensitive to salt content and perhaps compatible with the produced oilfield brine If this trend does continue and chemical solutions can be prepared in brines supplied by a brine aguifer and the oil reservo the presently foreseen socioeconomic impact of freshwater demar will be alleviated. If it is not possible to use oilfield brines for all of the chemical solutions by the time EOR proces are developed on commercial scales, a close analysis of water availability and negotiations for allocation will be required prior to implementation.

Thermal Processes Three types of thermal processes have currently gained

widespread recognition: (1) the steam soak process, (2) steam drive, and (3) in situ combustion. Processes using steam are viable commercial enterprises for viscous oils in California where approximately 250,000 barrels of oil are produced each da by steam injection. DOE will soon conduct some pilot field studies in the mid-continent region to use steam for enhancement of oil recovery from deeper, less viscous oils than those of

Steam Soak: This process involves the injection of steam for 10 to 30 days, followed by a shut-in period to allow for he transfer and penetration of the steam. The wells are then open for the production phase of the process, which may last as long as 6 months. The actual duration of the periods of injection, soak and production depends on the characteristics of the oil,

formation, and experience of the operator.

California.

products of distillation, and gas expansion. Condensation of steam produces a zone of hot water that behaves as a hot wat flood. The maximum anticipated oil recovery from the commer projects now in progress is about 50 percent of the reservoi in place. Environmental Aspects of Steam Stimulation: The steam

processes require a constant source of fuel to generate stea along with an ample source of fresh water. Crude oil produc from the field, natural gas, processed fuel and coal are use steam generation based on availability, economics, and air p tant emissions. Water requirements depend upon the process use, total amount of steam required, and the ratio of the am of injected steam (as equivalent amount of water) to the amount of oil produced, which may range from 0.1 to 5.0, or more. requirements gradually increase as depletion occurs. The actual pollutant emissions from steam generation de on a large number of variables such as the type of fuel and chemical composition, the efficiency of heat exchange, design

the boilers and stock, and meteorology. If produced oil is for fuel, approximately one-fourth of the production is cons in producing steam. Emissions from a 50MM Btu/hr boiler may include: SO₂ (10-25 kg/hr), NO_y (2-10 kg/hr), solid particu (1-3 kg/hr), unburned hydrocarbons (0.2-0.5 kg/hr), and CO (1.0 kg/hr). These are very broad ranges, but it is not poss

to present exact figures without measuring a specific instal over a long period. However, one can realize from the data steam stimulation processes add a potential, and real, airpollution hazard arising from direct-fired boilers. Since t total amounts of these pollutants must be maintained below S and Federal emission standards, the use of steam is constrai by the particular environmental standards involved. Perhaps constraint could be lifted if the boiler flue gases can be c pressed and added to the steam line, or injected separately

the oil-producing zone, to assist in production of the oil. DOE has a contract with the Carmel Energy Co. to test s a process in Kansas. The Vapor Therm process is designed to recover heavy oil by injecting a mixture of gases and steam reduce the viscosity of the oil, dissolve carbon dioxide gas

the oil, and increase the reservoir pressure. The hot combu gases (3,500° F) flow from the burners into a drum containin

water where steam is generated by direct contact of the hot combustion gases with the water. The steam combined with the

also acts as a scrubber for the combustion gases. The water removes corrosive components which are neutralized prior to injection of the steam. Many of the solid and corrosive components in the exhaust gas are trapped and neutralized in the ste Although small amounts of the water in the steam drum mu be removed regularly, atmospheric pollutants are almost entirel eliminated and beneficial results to oil production are obtained from injection of the combustion gases. The demand for fresh water is a major consideration of steam-injection processes since water containing salts cannot be used because of severe, irreversible damage to the boilers. The steam is employed to improve the mobility of viscous crude oils

that cannot be produced by other known techniques. Tests are also being designed to determine the feasibility of using steam drive processes for enhanced recovery of less viscous oils in t

compatible with regional water availability to municipalities a

agricultural interests; therefore, this is a major initial

mid-continent region.

In all cases, the demand for water must

compustion products is injected at the wellnead at 350,-650, F. In addition to its function as a steam generator, the water dru

consideration for all proposed steam-injection projects. There are several other environmental concerns associated with steamdrive processes in addition to air emission from the boilers an the water demand. Large amounts of produced water must be separated from the oil, treated, and disposed of in accordance with existing state pollution-control regulations. Produced oi emulsions are frequently difficult to break and require special treatment for resolution. The entrainment of oil from oil-wate separation and emulsion-breaking systems also requires close control because of the adverse effect it has on the waterdisposal system. Provisions must also be made for disposal of solid wastes from scrubbers, boilers, tanks and flow lines. In Situ Combustion: Several fire-flood pilot studies were made in the mid-continent region in the decades of 1950 and 196 but at the time they proved uneconomical and did not attain

commercial prominence. However, the pilot studies were very important in development of theories and technology unique to t process. The in situ combustion processes are based on generation of heat within the reservoir by burning some of the oil in the One procedure is simply the injection of air into a

well followed by ignition of the oil and continued injection of air as the burning front expands radially around the well. Неа at the burning front (800°-1,200° F) produces steam, coke,

destillation of the oil, thermal cracking of some of the heavy ends and pressure to move the front toward peripheral production

of the oil and furnishes the driving energy to move the oil the production wells. Other methods involving the transfer heat to the oil zone by water are employed, (such as altern injection of air and water) but detailed analyses of these beyond the scope of this paper. Air emissions from a well-designed in situ fire flood The thermal cracking reactions at the hot combust front produce light hydrocarbons that may escape during protion at the surface along with some carbon monoxide, carbon dioxide and sulfur dioxide. However, the larger portion of compounds probably remain confined in the reservoir. NO, p tion generally is absent because the lower burning temperate does not favor their production. Water produced with the crude oil can contain signification quantities of metals and metal oxides dissolved in the acid:

because the largest amount of heat dissipation, or transfer the reservoir, occurs behind the burning front. The heat is burned-out zone behind the front is of little value, but ot methods have been devised to improve the heat transfer to to zone ahead of the burning front. One method that has gained recent prominence is the wet combustion process. After the burning front reaches a predetermined size, water is inject place of air to act as a medium to transfer heat from the bout zone to the oil zone ahead. After an initial transfer heat as steam, the burned-out zone is cooled. Continued in of water results in a hot-water drive which reduces the vis

Gas Flooding

These can cause contamination problems through spil

and from leaks of the acid waters while they are being processon the surface for subsurface disposal. The pH of the reservater may be lowered to 2.5, enough to cause severe corrosic well casings in plugged (abandoned) wells and may lead to contamination of other aquifers communicating with the fire-flooil reservoir through the corroded segment of the abandoned

Any process employing, or producing, a gas has a potent

for air pollution which may be local (confined to less than acres) or regional (covering several counties, or an entire

state). Gas flooding is the introduction of gases, such as hydrocarbons and carbon dioxide, into the petroleum reservoi hope ficial and the petroleum reservoi hope ficial and the petroleum reservoi hope ficial and the petroleum reservoi hope ficial and the petroleum reservoir hope fici

improve oil-recovery efficiency through several theoreticall beneficial effects: (1) The injected gas increases the reservoir pressure, furnishing energy to drive the oil to production with the oil it is the oil to production with the oil it.

(2) By dissolving in the oil it reduces the viscosity and de of the oil and improves the mobility (ease with which the oil

may be injected directly into a gas cap above the oil zone to furnish a reserve of displacement pressure.

Before a decision to use gas flooding is made, a large, co stantly available source of inexpensive gas must be near the oi field. Examples are a producing gas field or a gas-processing manufacturing plant producing one of the required gases as a by product. The gas can be transported to the field by pipeline, truck or railroad tank car.

Transportation of the gases to the field by pipe, truck or rail is under strict regulation by both State and Federal statu An accidental spill, or large leak, from any of these sources me cause severe local hazards including the possibility of a fire or explosion, but dissipation and dilution in the atmosphere wi remove the hazard. One must also consider the fact that a viable economic incentive exists for not losing the valuable commodity

Water may be injected in large quantities in addition to t

being transported.

recovery process. The water is obtained from the produced water and recycled with added water obtained from a brine aquifer or nearby source of surface water. The water is generally treated for removal of solids, adjustment of pH, oxygen removal to reduce corrosiveness, and bacteria growth.

Air emissions at the field will generally originate from power facilities such as diesel or natural gas engines used in

gas requiring the treating and processing of large volumes of water at the surface similar to operations of a secondary

power facilities such as diesel or natural gas engines used in generating electrical power. Some hydrogen sulfide may also escape from the water-treating facilities. Other minor emission may originate from storage tanks, vapor-recovery units and heat treaters.

The potential for surface or shallow ground water pollution is the same as discussed previously for any field project processing large quantities of brine at the surface for reinjection Stored or impounded brine may leak, field pipelines may develop leaks, and well casings may crack or corrode during injection a production operations causing ground-water contamination. The potential of leaks and pipeline breaks have long been recognize as a result of secondary oil production. Because of strict Staregulations, equipment design and constant monitoring, the likelihood of leaks and spills during enhanced oil-recovery operations is considered less than for conventional operations.

compressed and injected into the formation from which it was produced as a pressure-maintenance technique as well as for disposal.

LEGAL ASPECTS

The Department of Energy has been mandated by law to as the environmental aspects of all EOR processes, and to assur that the commercialized EOR technologies are environmentally acceptable. The EOR projects are required to meet Federal, and Local laws, regulations and standards. In this context,

be placed in a pipeline if the hydrocarbon content is sufficed or it may be burned if the nitrogen and sulfur content will exceed ambient air-pollution standards, and the quantity pro is not sufficient to be of commercial value. Finally, it may

and Local laws, regulations and standards. In this context, laws are those regulations for the enforcement (by agencies as the EPA) of standards established under the laws.

The National Environmental Policy Act of 1969 (NEPA), P. 91-190, requires Federal agencies to consider the environmental actions that may affect the environment and to prepare Environmental Impact Statements for any major Federal actions that have a potential for an adverse effect on our environment

mental Quality which presents guidelines to Federal agencies respect to policy, responsibilities, planning and response elements, operations and coordinating instructions. DOE's NI implementation guidelines provide for an ongoing and continue environmental appraisal and review process, including the prearation and publication of EIS.

To implement the act, NEPA established the Council on Environ

The Clean Air Act and its amendments of 1970 and 1977 (I 91-604 and Pl 95-95) vested implementation authority in the administrator of the EPA. Each state has the primary responsibility for assuring air quality within the state. EPA is instead to compile a list of air pollutants to which the Act appl prepare air-quality criteria, and determine ambient air standards.

for pollutants listed in the air-quality criteria.

EPA regulations implementing PL 91-604 include the National Quality Standards (NAAQS) Primary and Secondary Ambient A Standards specified for sulfur oxides, particulate matter, camonoxide, photochemical oxidants, nonmethane by droom have

monoxide, photochemical oxidants, nonmethane hydrocarbons, an and storage of hydrocarbon.

some cases. Compliance is site specific and can change if the standards are changed. Under the Clean Air Act Amendments recently passed by Congress, areas which have not attained NAAQS must do so by December 31, 1982. To achieve this goal, EPA is promulgating an emissions offset policy. Under this policy, no increase in emissions will be allowed unless there is a corresponding reduction in emissions from existing sources.

The Clean Air Act Amendments of 1977 allow states to prevent degradation of air quality by SO₂ and particulates where air

quality is superior to the NAAQS. Under these provisions, states are allowed to classify their regions into three zones: Class I Regions (with very clean air) where only extremely small

emission sources are permitted, Class II Regions where new sources with moderate emission sources are permitted, if the combined effects of all sources do not exceed the allowable increments of air-quality deterioration, and Class III Regions where emissions from new sources are allowed to the extent of

in areas such as California where the standards are exceeded in

compliance with the NAAQS. Since many of these regions have not yet been designated, it is difficult to determine whether EOR target regions will be subject to air-quality provisions that ar too stringent, given the current environmental control technolog for the processes.

New Source Performance Standards are also changing. For example, prior to passage of the Clean Air Act Amendment of 1977 EPA set a tentative deadline of February 1978 for proposing New Source Performance Standards for coal-fired boilers, which may apply to boilers fired by other fuels as well. The proposed standards cover particulate matter, sulfur dioxide, and nitrogen

oxide emissions. Preliminary information indicates that standar will be proposed for small boilers which are the most common for EOR steam processes and are not currently regulated. Depending on how stringent the regulations are, new boiler installations may be required to add control technology not previously used at

steam-injection sites. Similar regulations could also develop for other aspects of EOR processes as well.

The Federal Water Pollution Control Act provides the framework for regulation of waste-water discharge to surface waters.

work for regulation of waste-water discharge to surface waters. A National Pollutant Discharge Elimination System Permit is required under this act before waste-water discharge to surface waters from any source. The intent of the act and the discharge permits is to require use of the best technology economically available by 1983 and to attain and maintain receiving-water

available by 1983 and to attain and maintain receiving-water quality adequate to assure protection of public-water-supplied water used for agricultural and industrial operations, and the

elimination System covering discharge permits and certification

A major objective of the Federal Water Pollution Control A was to prevent the discharge of pollutants into navigable water the contiguous zone and the oceans. The discharge of oil is prohibited, but under the provisions of the act pollutants do not include the injection of water, gas and other materials in wells to facilitate production of oil or gas. The regulation of oilfield operations is left to authorities within the oilproducing states. Therefore, the various states retain control of the injection of fluids in enhanced oil-recovery operations

EOR activities may be regulated under the auspices of the Safe Drinking Water Act. Enhanced oil and gas-recovery proces are given special consideration under this act. The law state that Federal regulations for the state underground injection programs may not prescribe requirements which impede any under ground injection for the secondary or tertiary recovery of oil and natural gas, unless such a requirement is essential to assure that underground sources of drinking water will not be endangered.

Although there are no Federal statutes, state water-use laws may present severe constraints to EOR development. Weste states water riparian laws are aimed toward defining allocatio for usage of the water resources. In essence, fresh water is limited supply and competing demands for it must be addressed through this system.

The Occupational Safety and Health Act provides for the protection of workers by assuring a safe and healthful work environment. The Department of the Interior Regulations related pollution control and waste disposal include leasee requirements against pollution of streams and surface or underground waters. The Bureau of Land Management obligates leasees to tareasonable precautions to prevent soil errosion, damage to forage and timber growth, air and water pollution, damage to fossils, historic and prehistoric artifacts. The Bureau also requires the leasee to fill sumps and other excavations, removed or cover debris, and to restore the surface to its original condition at the end of field operations.

a considerable data base to: (1) assure compliance with state and federal laws, regulations and environmental standards, (2) to insure that a minimum of environmental disturbance occurs as a result of the EOR program, and (3) to alleviate any accidental environmental damage that might occur.

The constraints to EOR development from laws and regulation water availability. Socioeconomic impacts, onvironmental monitor

water availability, socioeconomic impacts, environmental monitor ing programs, etc., are being assessed. In addition, some areas of research have been initiated to develop specific data. These will be described briefly.

Research has been initiated to determine the rates and pro-

ducts of decomposition of the chemical compounds used for EOR under laboratory-simulated subsurface conditions. This work wil be used to analyze the long-term viability of the large quantiti

of EOR compounds injected during future commercialization of EOR technology. As a companion to this work, the dispersion and chromatographic properties of the EOR compounds are also being investigated under simulated reservoir hydrological conditions. These data will be employed to predict the long-term migration properties of the injected EOR compounds.

Biological degradation rates of EOR compounds by various cultures of bacteria is also under investigation. The data will

shallow aquifer. Information on the degradation kinetics of specialized cultures may be useful to actively degrade spilled EOR compounds by innoculation with specially cultured bacteria.

The transport properties and natural chemical degradation rates of EOR compounds in shallow aquifers is also being studied

be used to determine the natural decay rate of EOR compounds which may accidentally have polluted a segment of land or a

to develop data that can be used to anticipate the migration pattern and decay of the compounds.

Studies are also being conducted to determine the circumstances under which the injected EOR compounds will initiate

stances under which the injected EOR compounds will initiate local seisimic disturbances. In a related study, the reactions of the EOR chemicals with the cementing and supporting matrix of sedimentary geologic materials is under investigation. Data derived from this study will be used to determine whether long-

sedimentary geologic materials is under investigation. Data derived from this study will be used to determine whether long-term contact of the chemicals with sedimentary geologic material will disaggregate the strata and cause land subsidence to occur.

Other research specific to environmental concerns of EOR is anticipated as noted in the Environmental Development Plan (2).

In the study of the environmental aspects of enhanced recovery, eight areas are of concern: Atmospheric emmissio water use, groundwater impacts, waste-water effluents, soli wastes, occupational safety and health, physical disturbanc These are being addressed for the overall EOR p in a Programatic Environmental Impact Statement now being p

Assessments of each field test site. Research has been ini in areas where scientific data are not currently available determine possible environmental consequences of commercial of EOR technology. Developments in Federal, State, and Local laws, regula-

pared. Each issue is also considered in individual Environ

and standards are being followed closely to ensure compliance DOE activities and to be informed as well as to assess the jected impact of the legal considerations on Enhanced Oil Recovery.

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SESSION 7 CONTROL OF FOSSIL FUEL POWER GENERATION — CONVENTIONAL

Chairman: William Mott

Co-Chairman: Bernard Baratz



K.E. Wilzbach, C.D. Livengood, and P.S. Farber

Argonne National Laboratory

The development of new energy technologies carries with it a responsibility to identify and evaluate appropriate environmental control technologies and/or strategies. In the area of coal utilization, a continuing program for this purpose is being sponsored at Argonne National Laboratory (Aby the Division of Environmental Control Technology, Assistant Secretary for Environment, DOE.

As part of the program, in-depth engineering and economic assessmen of available and near-term control technologies have been made by the ANL staff and several subcontractors. The topics covered include coal cleanin NO control, particulates collection, flue gas desulfurization and denitrification, low-Btu gasification with combined-cycle generation, and solvent refining of coal. The development of advanced technologies, such as MHD and fuel cells, is being monitored in-house together with such other fuel cycle elements as coal transportation.

Another important aspect of the program is the comparative evaluation

of different control technologies. To facilitate this effort, an extensive data base of coal properties and reserve amounts has been established. Al information to yield data from which estimates of cleanable reserves can be attempted. In order to use this large volume of data efficiently and speethe assessment task, computer models of control technologies are being developed for incorporation into a systems analysis framework representing t coal fuel cycle. To date, this framework has been used for several case studies of different power generation scenarios. These studies have inclu both eastern high sulfur coals and western low sulfur coals, and have util ized plant sites consistent with current practice. The comparisons have determined the least-cost mix of coal type and control technologies needed to meet current environmental regulations at each site, while at the same time producing electricity at minimum cost. Costs and energy usage for environmental control have been derived with respect to a reference 500-MW power plant. The effects of proposed regulatory changes have also been investigated and have been shown to produce significant increases in both power costs and energy usage for environmental controls.

At present, the ANL comparative assessment model is only applicable conventional combustion techniques. As performance and economic data beconventional combustion techniques such as fluidized bed combustion, MHD, limitaction, and gasification/combined cycle systems, this information will be incorporated into the comparative assessment model. Once this incorporation has been completed it will be possible for the Department of Energy, other interested users, to evaluate the effects of these technologies on power generation while meeting environmental regulations on a site-specific

TECHNOLOGY FOR COAL-FIRED INDUSTRIAL BUILDERS

T. W. Sonnichsen, R. E. Thompson, KVB, Inc.

and

H. Huang, Argonne National Laboratory

This paper is a synopsis of a study conducted for Argonne National Lab

to examine the effectiveness of combustion modification methods for NO applicable to coal-fired industrial boilers including low excess air, combustion and burner modifications. Boiler types considered included

and underfed stokers, spreader stokers, pulverized and cyclone fired u

Baseline (as-found) NO emissions from grate fired stokers were shown the range of 200 to 300 ppm. Similarly, as-found emissions from suspefired units were quite low as compared to comparably designed utility Low excess air was shown to be the most effective method on existing u emissions by approximately 10%. Evaluation of staged combustion and b fication, however, were limited due to current boiler designs. Major

modification/design and implementation are necessary before the potent techniques can be fully evaluated.

The study emphasized the numerous operational factors that are of major to the user in selecting and implementing a combustion modification incenergy considerations, incremental capital and operating costs, corros

secondary pollutants and retrofit potentials.

THE LOW NO $_{\rm X}$ HEAVY FUEL COMBUSTOR CONCEPT PROGRAM John R. Facey

U.S. Department of Energy Energy Technology

and

Richard W. Niedzwiecki NASA, Lewis Research Center

The objectives of this program are to generate and demonstrate the technology required to develop durable gas turbine combustors for util

and industrial applications, which are capable of sustained, environment acceptable operation with minimally processed petroleum residual fuels. The program will focus on "dry" reductions of oxides of nitrogen (NO)

or shale); acceptable exhaust emissions of carbon monoxide, unburned hydrocarbons, sulfur oxides and smoke; and retrofit capability to existing engines.

ASSESSMENT OF ENERGY AND ECONOMIC IMPACTS OF PARTICULATE CONTROL TECHNOLOGY IN COAL-FIRED POWER PLANTS

V. Ramanathan

S. Reigel
P. Gorman

P. Reider

Midwest Research Institute

Midwest Research Institute has carried out a project, under a contract with Argonne National Laboratory, to assess the economic and energy impacts of particulate control systems in coal-fired power plants. The assessment was based on major functional variables such as plant size (100 to 1,000 MWe), location, coal type, and emission standards. The work on this program resulted in the generation of algorithms, to predict equipment cost, instal-

lation costs and energy usage for various particulate control devices. The devices considered were electrostatic precipitators (hot side and cold side)

fabric-filters (reverse air and shaker types) and wet scrubbers.

First, a boiler performance model was developed using variables such as plant size, coal characteristics, etc. The output from this model (i.e., flue gas flow rate, grain loading, etc.), then was utilized in control device performance models to generate required design and operating parameters for the control systems under study. These design and operating parameters were then used in the cost models.

The cost models aggregate three cost items: the first costs (capital investment), total first-year annualized costs and the integrated cost of ownership and operation of the control equipment over an assumed plant lifetime of 30 years. The models have been programmed for speedy computation. However, the algorithms are easily solvable with a hand calculator. In additional control of the cost of the c

tion, suitable guideline values have been provided for independent variables wherever necessary. Ample case studies are presented to demonstrate use of the models.

Harvey M. Ness and Stanley J. Selle

U.S. Department of Energy Grand Forks Energy Technology Center

Fly ashes from the combustion of many Western and Gulf Coal lignites and bituminous coals contain high concentrations of alkali which can be used wet scrubber for removal of SO₂. Additionally, dry methods of flue gas furization will be required for new and retrofit power installations in water-scarce areas in the Western U.S. The Grand Forks Energy Technolog of DOE has performed tests on utilizing fly ash in lieu of lime/limestor 130-scfm laboratory scrubber and a 5000-acfm pilot scrubber operated on gas slipstream at a utility burning North Dakota lignite, and on dry son

and injection techniques in a 75-1b/hr pulverized coal-fired pilot combutance of the composition of the composition of the coal and alkali in a wet scrubber; and 2) a series of tests designed to evaluate the coal and naheolite as dry sorbents for SO_2 control. Ash alkali wet scrubber include the correlation of SO_2 removal, alkali utilization, and scale formation with operating conditions such as feed stoichiometric respectively. Inquid-to-gas ratio (L/G), pH, and the concentrations of suspendissolved solids. Results on dry absorption of SO_2 include injection in flue gas with subsequent collection in 1) a pilot ESP, and 2) a pilot be conditions; the points of injection ranged from direct addition into the along with the coal, to addition at the inlet of a cold-side ESP or baging Data on SO_2 removal efficiency and reagent utilization are correlated we conditions. A parallel laboratory study on the kinetics of reactions be

the dry sorbents and flue gas SO_2 and NO_2 are also described.

Meyer Steinberg, Anthony S. Albanese, and Vi-Duong Dang

Brookhaven National Laboratory

C. F. Baes, et al, Oak Ridge National Laboratory

Gregg Marland, Institute for Energy Analysis

The possible adverse global environmental effects of CO₂ buildup due to fossil fuel energy utilization have prompted an investigation of possib methods for its control. A systematic overview is presented for various routes for removal, recovery, disposal and use of CO₂ from various control points in the global system. The effect of substitute alternative non-fos energy sources on the global CO₂ problem is evaluated. The energy and mass balances for a number of removal and recovery routes are used as evaluation criteria. Flow sheets are presented for conversion of CO₂ from various sources to synthetic carbonaceous fuels with the use of non-fossil energy. Several unique CO₂ disposal alternatives are presented and discussed.

THE IMPACT OF COGENERATION UPON EMISSIONS

Eric Lister

U. S. Department of Energy Energy Technology

The objective of this paper is to highlight why an energy conservation technique such as cogeneration is of primary interest to a Fossil Energy group whose major criteria for success is the utilization of coal. The paper will show the following:

- 1) That cogeneration can reduce the emissions/useful output by a factor of 3 to 5 and is therefore one of the leading technologies for the acceptable utilization of coal and coal-derived fuels.
- 2) That if cogeneration on coal and coal-derived fuels is to become prominent in the industrial and commercial/residential sectors it will require the continual development of (a) heat engines to handle the harmful agents in these fuels (b) heat recovery equipment so they can be cogenerated and (c) an on-going effort to identify and develop other critical technologies needed to make coal cogeneration the success that it promises

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K.E. Wilzbach, C.D. Livengood, and P.S. Farber Argonne National Laboratory

1 INTRODUCTION

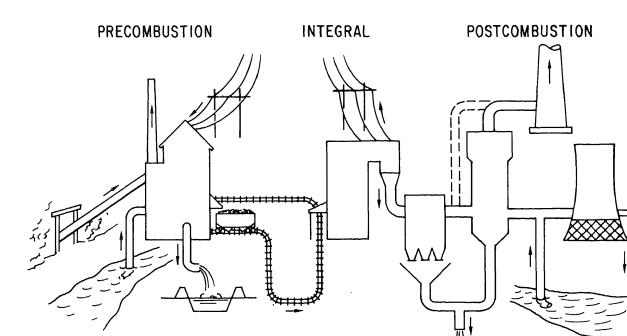
The Environmental Control-Coal Utilization Program is a continui

Argonne National Laboratory (ANL) effort sponsored since 1976 by the Division of Environmental Control Technology, ASEV/DOE. It provides in-depth evaluations of the technical, environmental, and economic aspects of control technologies for coal-based energy systems, as well as systems comparisons alternative control technologies and/or strategies. The program was developed in response to a need within ERDA, predecessor to DOE, for independent evaluations of the capabilities of existing technology and reviews of ongoinesearch and development programs. In this way, the program assists to Environment staff in fulfilling its responsibility to assure the adequacy environmental control systems for fuel extraction, conversion, and utilize

Subjects under evaluation span the coal fuel cycle from mine mouth waste disposal, as shown in Fig. 1, and include both current and developing

tion.

ENVIRONMENTAL CONTROLS



realize that while these subdivisions are convenient of the system. The niques are truly independent of other parts of the systems are in fact so pervasive and far-reaching that a systems analyst demanded for a complete assessment of any of the components.

This systems perspective, coupled with the use of in-depter analyses, places the ANL program in a unique niche within the assessment efforts, being both more comprehensive than studies a single control technique or pollutant and more detailed that gional or national energy assessments. Our approach begins with information on the costs, reliability, energy requirements, and secondary effects of pollution control systems from report sions with manufacturers, users, and developers of the process effort, the capabilities of the in-house staff are supplemented able use of subcontractors and consultants with special cap expertise. Evaluation of this information leads to the idem problem areas, inherent process limitations, and high-payoff

search and development.

Further, the information on individual processes is part to technology comparisons that use a computerized systems—a odology. These comparisons are used to identify the potential rechnologies as a function of environmental regulations, location of development. In cases where several approaches appear to be it is often possible to identify critical process parameters most effective in altering the existing balance or that are small changes in environmental requirements.

The initial studies performed in the program were devoto surveying available technologies/strategies for the copollutants (SO_2 , NO_{X} , and particulates) from coal-fired utilities were presented in our first report, ANL/ECT-1, together of existing federal and state environmental regulations and the fects of pollutants. Some attention was also given to the compollution, disposal of solid wastes, and the status of fluid bustion (FBC) technology. Information gathered in that fix studies has subsequently been used to identify and scope massessments performed by subcontractors to ANL, resulting in series of reports dealing with individual control technologies. With these studies, the ANL staff has been analyzing areas technology not previously covered and has begun to study advantage.

series of reports dealing with individual control technolgies. with these studies, the ANL staff has been analyzing areas technology not previously covered and has begun to study advant under development. All of these assessments are briefly refollowing section. The third part of the paper presents the typical technology comparison based on alternative regulators.

The technology assessments performed to date have focused of able and near-term technologies in order to establish an informat suitable for technology comparisons and for the evaluation of defenvironmental regulations that may affect coal-based energy systems data will also serve as benchmarks in analyses of mid-term technology such as the studies are now being developed by the program staff be noted in the following discussion.

2.1 PRECOMBUSTION CONTROLS

Precombustion, as defined in this program, encompasses all of from the mine mouth up to the fuel utilization step (the boiler, in tional systems). It can range from a simple conveyor belt and stor in the case of a mine-mouth plant to complex arrangements involving stages of transportation and storage coupled with coal conversibility and storage form.

2.1.1 <u>Coal Transportation</u>

Transportation facilities (rail, barge, truck, pipeline) ar significant in determining both the availability and delivered specific coals or coal products. Thus, the fuel choice at a particular, through the fuel characteristics, the selection of environment trols can be influenced by the transportation system. There may a significant consumption of fuel or other resources and production tants during transport, although the latter are admittedly widely dist

However, these transport-related pollutants will become more notic

An extensive survey of the available literature on coal transplants been made by the program staff with particular emphasis on environments and costs. This information will be incorporated into future tive systems evaluations.

the system evaluation as on-site emissions are lowered.

2.1.2 Coal Preparation and Cleaning

By far the most extensive effort in the precombustion area an assessment, performed by Bechtel Corporation, of coal prepara cleaning technology. That study addressed current industry pract developing methods for both physical and chemical cleaning, as well effects of cleaning on important coal properties. Detailed flow she used to generate estimates of costs and environmental impacts due to specific coals. Although the results were far too comprehensive to see the co

here, one can conclude that significant sulfur reductions are poss carefully selected coals if fine-coal cleaning is employed. However technique carries with it potential environmental problems in the dev reserves were matched with washability data and merged into a sir production.

2.1.3 Solvent Refined Coal (SRC)

duct) and SRC-2 (liquid product) technologies. A preliminary s literature and pilot plant results for SRC-1 was performed for ou Air Products and Chemicals, Inc. That project also included de product costs and material and energy balances for a 20,000-tonsfeed plant. Product costs were estimated at about \$3.25/106 Btu for a delivered coal costing \$25 per dry ton. Finally, the p SRC-1 as a fuel were discussed relative to conventional pulverize need for some burner redesign was identified, as was a potential high NOx emissions.

This included 35% of the reserves that account for 80

More extensive coal processing is represented by the SRC-1

A more recent study conducted by the ANL staff surveyed e monitoring results obtained at the Ft. Lewis pilot plant. No meeting existing air and water standards were identified, but the of the plant and the limited testing data available preclude any sions at this time.

2.1.4 Coal-Oil Mixtures (COM)

The use of COM has been widely discussed as a potential fu ing boilers. It would further the nation's goal of greater coal while, it is hoped, creating minimal environmental problems. study of this technique by the program staff has revealed hi degrees of success in producing, storing, transporting, and firi ways in which different oil and coal properties affect the COM :

the consequences of prolonged use are not well-defined.

Some add-on flue-gas cleanup controls will probably be COM use, but the requirements will vary with the sulfur contents and oil used, as well as their relative proportions. This is du that the applicable regulations are generally a combination (on cent basis) of those for coal and oil taken separately.

2.2 INTEGRAL CONTROLS

Taking advantage of inherent system characteristics to ronmental control goals is obviously attractive insofar as it re excluded as an adequate stand-alone technique by the percentage requirements of new environmental standards. The other integral options studied by the ANL program and described in this section viable, but their vulnerability to regulatory change should not looked.

2.2.1 Combustion Modifications for NO_v Control

An analysis of combustion modification techniques for NO_{X} utility boilers was performed by KVB, Inc. It identified staged and low-excess-air operation as the most cost-effective methods founits. For new units or extensive retrofits, improved burner defound to offer promise of even greater reductions. There is covariation in the NO_{X} -reduction potential between various combinability type and combustion modification, but the reductions now a commercial units are generally less than 50% and typically only 20-3

ational concerns are centered mainly on unresolved questions about

KVB is presently developing an update of this report to incl opments in the field during the past year. Also, they have rec pared a similar study of NO_X control through combustion modific industrial boilers. Similar techniques are used, but the analysis cated by the wide variation in furnace types and sizes. This wor tiated in anticipation of increased policy interest and regulator related to the industrial use of coal.

2.2.2 <u>Fluidized-Bed Combustion (FBC)</u>

arising under these operating conditions.

The possibilities inherent in FBC for integral control of S while providing economic power for utilities and industry have b discussed. The strong base of information that exists at ANL for nology has enabled the program staff to develop assessments of FBC ties and existing or potential problems. One such study is now ition.

However, in order to obtain an independent point of view, M

oration has been engaged to analyze results reported at the 5t tional Conference on FBC held in December 1977. They have had access to these data as conference organizers. The method used be unique in the way data, issues, problems, and information gaps sented in matrix form. Also, it uses a linear approach to conclus opment that is independent of prior knowledge regarding issues or This may be regarded as either a strength or weakness, depending needs. This work is now nearing completion.

the above gasifiers, a Texaco unit is being included in this stud both Illinois bituminous and low-sulfur Montana subbituminous coals used in the analyses. This work is now nearing completion. Both studies have found the G/CC systems to emit lower qua pollutants than conventional power plants and to be economically of with existing technologies. However, the wide band of uncertai associated with these cost estimates precludes any firm conclusion This uncertainty is largely due to the need for further development of both gasifiers and the advanced high-temperature ga required. These developments will be crucial to commercialization technology, since significant cost advantages must be shown before novel approach will be accepted by the utility industry.

Assessments of two additional coal utilization technology

porating integral controls are now being planned. Advanced molter

promise of high efficiency. An upcoming study will explore nu

(IGT), and entrained-flow (Foster wheeler) gasiliers produce

has been undertaken by United Technologies Research Center. In a

With this work as a basis, a more extensive

2.2.4 Other Developing Technologies

and Montana coals.

fuel cells may offer unique siting opportunities as well as highly coal utilization. The cells are generally viewed as environmental but the environmental control aspects of the fuel conversion proce relationship to the fuel cells merits analysis. Power plants based on magnetohydrodynamics (MHD) also

answered questions regarding the efficiency of both integral a environmental controls for this technology.

2.3 POSTCOMBUSTION CONTROLS

Most questions about environmental controls have been cente costs and effectiveness of postcombustion cleanup systems. For th a very significant part of our program's effort has been devote area.

2.3.1 Particulate Collection

Several studies have been devoted to the assessment and m particulate collection systems. The first of these, conducted b Research Institute, discussed the sources and characteristics of

applicable emission regulations, available technologies, technic

on a combination of emission regulation, coal sulfur and ash content characteristics.

In order to further explore the tradeoffs between differen Midwest Research Institute was engaged to develop energy and econo

of available particulate collection equipment suitable for our of That model supplements a previously developed comput written at ANL (see Sec. 3.1). Another study was performed at Manhattan College with th assessing collection techniques for fine (submicron) particula

Particles in this range are of great concern, because they are resp may carry toxic trace elements. Topics addressed in the study in formation and characterization of fly ash for different coal and bot the performance of both conventional and novel devices, and energy,

and operational aspects of the alternatives. Baghouses were ide the most attractive option among available alternatives as emission are tightened, although ESPs may be competitive for high-temperat

pressure applications. Novel devices under development were judge little promise for improvement in fine-particulates control befo best. At the present time, we are sponsoring a study by KVB, Inc.

tigate any correlations between combustion conditions and particul in a better understanding of how particulate control is influenc and combustor characteristics.

2.3.2 Flue Gas Desulfurization (FGD)

fired with high-sulfur coal.

No other area under the purview of this program has been t of such controversy as FGD. This is due to a number of factors, strong regulatory pressure for development, a limited base of exp utility applications, and the lack of firmly established "standar or design procedures that consistently produce satisfactory pe

A study surveying the status of FGD, worldwide as well U.S., was performed for us by the Tennessee Valley Authority (T

than 20 different process types were identified. These were divi equally between those yielding throwaway and recoverable products. the only significant experience in this country is for throwawa

limestone (L/LS) systems, which comprise about 95% of the opera systems on a megawatts-served basis. The study identified nume ational problems and high maintenance requirements for these s

If sufficient data are found to be available, this study w

pointed out that there is as yet very little experience with FG

Subsequent projects by both TVA and Batelle Columbus L have cought to utilize the available data to model performance as If regulatory requirements for NO_{X} reduction in stationa are increased, the combustion modification techniques noted in Secono longer be adequate. In anticipation of such a possibility, we KVB, Inc. to include in the NO_{X} -control study mentioned previous tion on gas-phase reduction of NO_{X} . Ammonia injection appears but large-scale coal-fired tests are needed to verify its effective investigate costs and secondary pollutants.

In another assessment, TVA reviewed processes currently be oped for the simultaneous removal of NO_{X} and SO_{2} from flue gases. such processes, most Japanese in origin, were evaluated in some demost advanced types were found to be dry selective catalytic redwet oxidation-absorption-reduction. However, further process descale-up, and application to flue gas from coal-fired boilers are before realistic assessments of their potential roles in the U. made.

2.3.4 Solid-Waste Disposal/Utilization

The question of solid-waste disposal has been reviewed by ANL staff and several subcontractors in connection with studies of late control, FGD, and FBC. In general, the concerns identified volved about cost, questions of land-use policy, and the possible water pollution through leaching. Passage of the Resource Conser Recovery Act (RCRA) has greatly increased concern regarding to question because vastly increased disposal costs could be in the of view of this area is planned pending an evaluation of the regulate formulated by the EPA.

2.3.5 <u>Waste-Heat Disposal/Utilization</u>

The disposal/utilization of power plant waste heat is right sidered as an environmental control technology, and one that has been the subject of considerable controversy. Assessments of the etal, performance, and economic factors associated with the variou techniques are now being planned to supplement preliminary data g the ANL staff.

The comparative assessments draw upon information generate detailed technology evaluations. These comparisons can involve t coal-to-power system, or they may focus on specific system elements particulate control. In order to provide this flexibility, approach is used wherein each module represents a significant, nically separable, component of the system. The modules are gradua computerized as sufficient data become available through the acqui development of models. Several computerized data bases are also in ment as sources of input information for the comparisons.

3.1 MODELS AND DATA BASES

One data base was the result of the effort described prev integrate coal reserve and washability data. At this time, integrate been achieved for 189 different state/county/bed combinations. How

A related data base has been developed using the Bureau of I serve and analytical data tapes. More than 56,000 separate entric

available in the base. The information is useful in providing coal analyses for the evaluation of control performance, identifying differences in coal characteristics, and assessing coal variability.

in the preceding sections. These efforts have included the entit generation system, FGD, and particulate control. been active in this area with the development of a particulate con incorporating cost and performance information for ESPs, bagho cremental electricity cost for each option as a function of coal p plant size, and regulatory constraint. An example of the program shown in Fig. 2 for a comparison involving a slightly cleaned, 1 eastern coal. Note that the most economic options in this case an

least-cost option for each regulatory alternative in the follo parison.

3.2 EXAMPLE COMPARISON

Recent months have seen a vigorous debate waged over the revisions to the federal New Source Performance Standards. For t we have developed a comparison of two plausible regulatory sce applied to the reference case described in Table 1. The environm

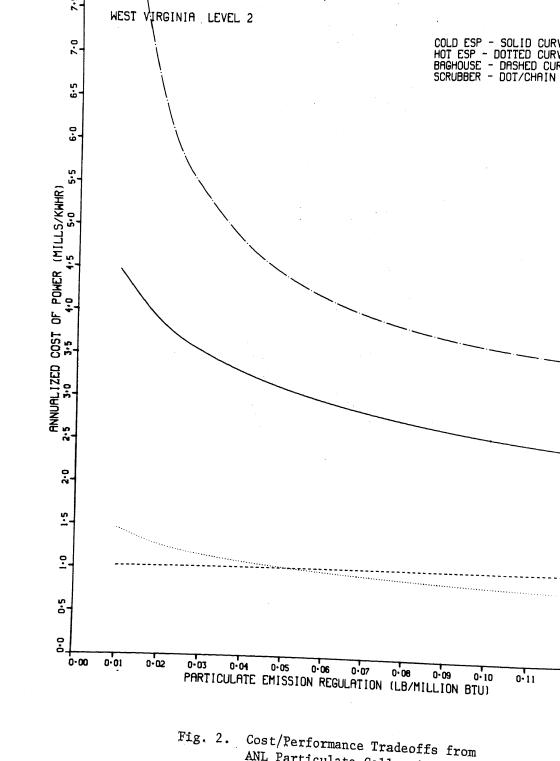
ESP and the baghouse, with the hot ESP favored under present NSPS (Btu) and the baghouse having a slight advantage under the propose NSPS $(0.03 \text{ lb}/10^6 \text{ Btu})$. This type of analysis was used to s

fact that many coals were tested more than once leads to a total of integrated data sets. Present plans call for significantly expar sample using additional washability information collected recently.

Modeling efforts by subcontractors to the program have been

The model calculates energy consumption, capital cost

The ANL staff



ANL Particulate Collection Model

				
	Location		Northern Illinois	
	Net outpu	t	500 MWe	
	Type		Conventional pulverized-coal fired	
	Heat rate		9200 Btu/kWh	
	Environme	ntal controls	None	
	Coal char (as recei	acteristics ved)	10,500 Btu/1b, 16% ash, 0.6, 1.0, 3.0, or 5.0% sulfur	
		Table 2. Envi	ronmental Controls	
1	Particulates	Lowest cost option chosen from hot or cold and baghouses.		
	so ₂	SO ₂ Limestone slurry FGD with com sludge disposal in a clay-1		
	$\mathtt{NO}_{\mathbf{x}}$	Combustion m	odifications.	
	Cooling		al draft cooling towers instead nce-case once-through cooling.	
	Water Treatment	System correst technology	sponding to the best available	
1 .	to different levels of with certain benefits tricity produced by the conceptually appealing vented at this time by lack of a consensus on sent the costs separate of power, residual post. Air pollution residual post different sulfur of greatest sensitivity for pond to the full scrub removal determined on	environmental to society, for the plant. How for arriving a uncertainties the costs of ely in terms of elutant emissi control levels or costs and p bing requirement the basis of	is to illustrate the costs cor l control. These costs are remost of which are the 500 M wever, while a cost-benefit are the optimum control level, is in pollutant-damage estimate health effects. Therefore, we f economic penalties applied tons, and the consumption of l for this example are shown i were used, since this is the performance. These alternative int recommended by the EPA, with either daily or monthly averaging used, as shown in Table 1	

Alternative NSPS:

NO_X

Particulates

SO₂

85% removal or 92% removal,
both with a maximum level of 1.2
1b/10⁶ Btu and a minimum require
level of 0.2 1b/10⁶ Btu

Pliance with the present NSPS with no additional controls, while a

fur some flue-gas bypass could still be used to eliminate rehe

ternative standards. The 3% sulfur level is representative of comany utilities and requires FGD in all cases. At 5% sulfur, the

Both of these low sulfur coals require full scrubbing un

0.1 1b/10⁶ Btu

1.2 1b/10⁶ Btu

"ceiling" comes into play since greater than 85% removal is require a level of 1.2 1b/10⁶ Btu. Thus, these four sets of coal proper yield a representative spectrum of SO₂ control costs under all of considered.

Based on the foregoing assumptions, the incremental electric (in 1980 \$) and pollutant burdens associated with the environment are presented in Figs. 3 and 4. Note that they are expressed as or 1b/MWh in order to more directly relate costs and benefits. format illustrates how, when regulations are based on energy in

Particulates

SO2

1b/10⁶ Btu), the addition of energy-intensive environmental cone pollutant can actually increase emissions for others. For inspection of Fig. 3 shows that the addition of scrubbing for SO₂ of increasing coal sulfur (under present NSPS) serves to increase of NO_x and particulates emitted, since the plant heat rate changes 9500 to nearly 10,000 Btu/kWh. This effect on performance is dramatically in Fig. 5, where the energy consumption due to control For low sulfur coals, the energy requirements for pollution contare more than doubled under the proposed changes.

The incremental economic costs shown in Fig. 3 are due prime increasing FGD requirements that result in both additional equi and large increases in the amount of solid waste requiring dispose in Fig. 4). It is clear from the figures that there is a trade electricity cost and pollutant emissions and that the change in f SO₂ regulation also changes the form of the cost balance. Und sent NSPS, emissions are fairly uniform across all coal types, an

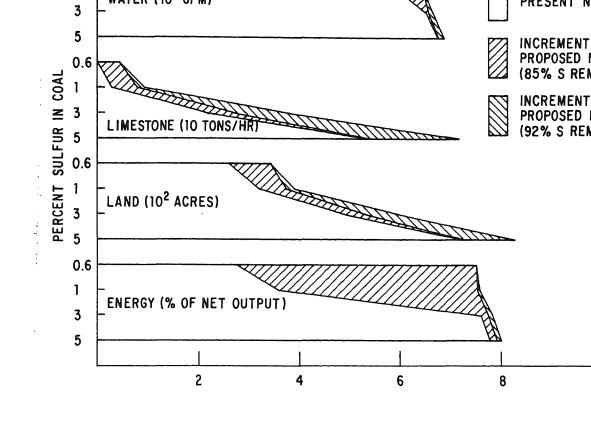


Fig. 5. Resource Consumption by Environmental Controls

other hand, a fixed percentage-reduction requirement for SO₂, couple very low "floor," greatly reduces the cost differential while product variations in emissions. This acts to favor the use of local coals areas of the country. However, where that implies a shift from low-sulfur coal use, air emissions will not be significantly reduced wastes will increase by a factor of 2-4.

delivered prices, the economics favor the use of low sulfur coal.

land-use impacts due to FGD are somewhat damped by the existing

Resource requirements, as shown in Fig. 5, also increase requirements are dominated by condenser cooling, so that the increa the addition of FGD is less dramatic than one might anticipate. this is a very site-specific item, and the choice of a less humid would result in increased water losses because of waste-pond eva The sludge pond is also responsible for the increases in land requirements closely follow the changes in solid-waste burden, since a considepth of about 20 ft was used in the calculations. Note that the c

ash disposal.

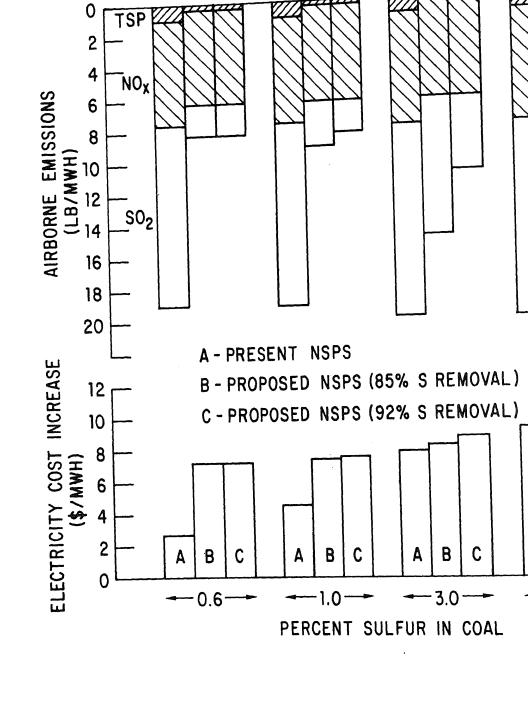
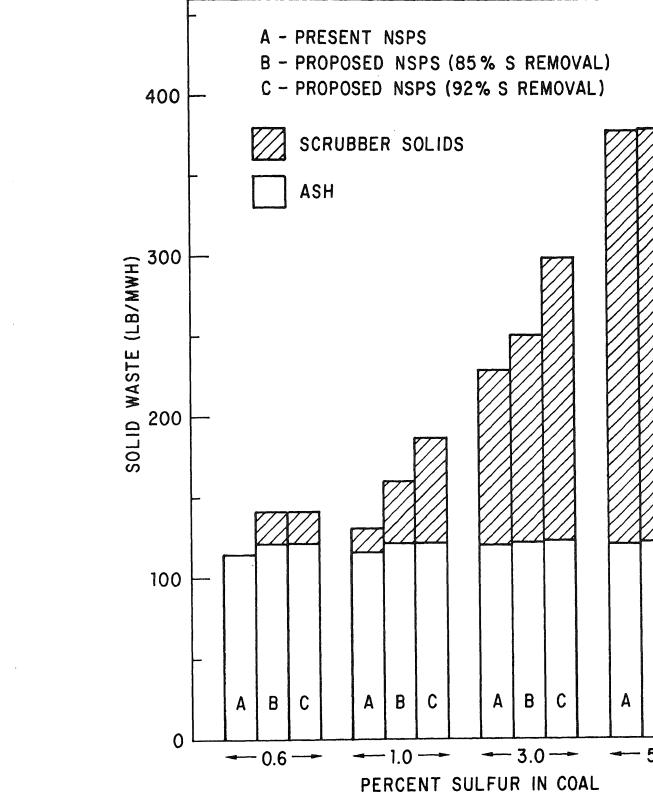


Fig. 3.

Environmental Control Costs and Residual Air Emissions



4 CONCLUSIONS

The preceding example has provided ample indications of environmental controls affect other parts of the energy system and (air, land, and water). If precombustion controls had been analmore far-reaching interactions would have been seen. Thus, it is that a systems perspective be adopted and faithfully followed in the performance of controls, the desirability of regulatory change environmental aspects of research and development programs.

numan and environmentar cob

The many tradeoffs between costs and benefits also argue p for basing emission restrictions on energy output rather than in would not only provide a more direct measure of the cost/benefit would promote the use of efficient controls and conserve resource viding an additional incentive for efficient plant operation. Fit could greatly enhance the attractiveness of measures to util energy, as in cogeneration. Figure 6 illustrates for particulate that emissions are presently a function of heat rate (plant efficient shown by the upper and lower lines. The middle line shows how a based on output energy ties emissions to the system benefit and effect, penalize less efficient plants by requiring greater r

Lastly, our assessments and comparisons indicate that the clear-cut choices and no panaceas in environmental controls for None of the developing technologies has such an economic advantage realities of cost escalation and market competition could not poss it to negligible proportions. In that case, experience has show dustry will opt for what is known best -- existing technology ticular, utility companies are quite conservative and intrins luctant to accept new technologies with uncertainties in commerciance and costs. This is not meant to imply that development systems should not be undertaken, but only that the performance potential of each approach must be scrutinized with great care and each stage in its development. Changing priorities, policies, at tions have the power to shift the cost/benefit balance far more questions.

any but the most unusual technological developments.

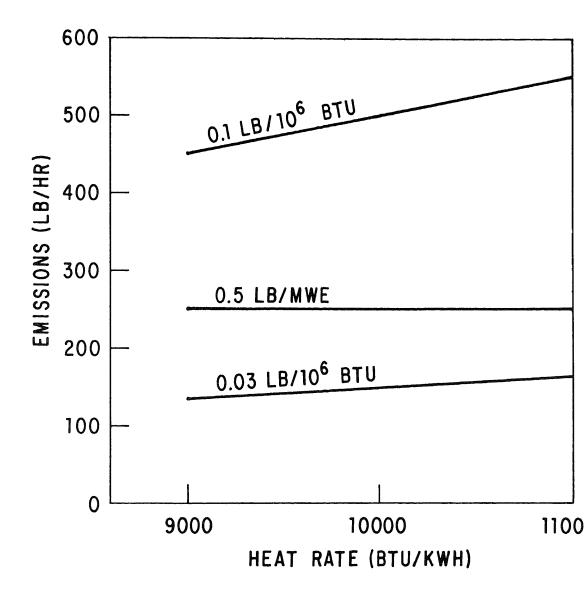


Fig. 6. The Effects of Alternative Regulatory Strategies on Emissions

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1. INTRODUCTION

Emissions from stationary combustion sources have been effectively to 10% or less of their initial levels for all major or criteria possessed NOx. The conversion of fuel-bound nitrogen to NO during the tion process makes the control of NOx emissions from coal-fired both particularly difficult. However, coal is our largest natural foss source and DOE is responsible for developing methods of utilizing environmentally acceptable manner. Coal is used extensively for protection by the electrical utility industry but the increased use of industrial applications cannot be ignored, particularly in air quatrol regions where NOx air quality standards are barely being met

Consistent with their responsibilities, EPA has established resear NOx emissions from coal combustion of 200 ppm by 1980 and 100 ppm is also currently assembling background technical support document yet-to-be proposed industrial boiler NOx emissions regulation.

For the reasons outlined above, a need existed to conduct a comprestate-of-the-art review of all potential combustion modification modification modification of control on coal-fired industrial boilers. Combustion modification the past been the most cost-effective approach to limiting NOx for emissions. With the resurgence of interest in spreader stoker unidesirable to document the most recent technical developments plus R&D needs associated with that boiler design category.

2. NOx EMISSIONS FROM COAL-FIRED INDUSTRIAL BOILER

NOx is formed during coal combustion from two sources: (1) the the fixation of atmospheric oxygen and nitrogen, and (2) the conversion bound nitrogen. The availability of oxygen, as well as temperature

^{*}This study was conducted for Argonne National Laboratory under Co. 31-108-38-3726 as part of an on-going program, Environmental Cont. cations of Generating Electric Power from Coal, being conducted in the DOE Division of Environmental Control Technology.

Total Total
ditions. Burner, grate and furnace configurations are important factors
NOx formation since they influence mixing patterns, heat release and abs
tion rates as well as residence times within the furnace.
Significant variations in firing methods and combustion conditions occur
in industrial sized coal-fired boilers. The smaller units (up to approx
mately 250,000 lb/hr steam flow) are largely stoker-fired units. They
differ primarily in the mechanical method of coal introduction into the
furnace, including overfed, underfed and spreader stokers. These units

furnace, including overted, underfed and spreader stokers. These units characterized by release and combustion of volatile materials above the and bed combustion of the resulting char on the grate. In spreader stok the coal is hurled into the furnace so that devolatilization and some pa combustion occurs prior to landing on the grate. In all stokers, the bu of the combustion air is supplied through the grate.

Larger boilers generally use suspension firing in pulverized or cyclone units. In these units the combustion air is supplied with the coal thro individual burners. Several configurations of pulverized-fired units ar These include tangential, single wall, horizontally opposed and vertical fired boilers. They differ primarily in the location, arrangement and t

of burners in the furnace. Other than size and the corresponding number burners, these boilers are similar in design to utility sized units.

DEPENDENCE OF NOx EMISSIONS ON BOILER TYPE

NOx emissions from industrial boilers are dependent on the boiler design primarily because variations in the type of combustion influence the cor version of fuel nitrogen. A summary of baseline (or as-found) emissions levels by boiler firing type is presented in Table 1.

Table 1.	Summary of Baseline NOx	Emission Levels
Firing Type		NOx Emissions, ppm (3% O2, Dry)

	NOx Emissions, ppm
Firing Type	(3% O ₂ , Dry)

Suspension Fired 800

Cyclone 350-900 Single Wall

500 Horizontally Opposed

400-500 Tangential

Vertical ___

Stoker

250-350

Underfed

200-300 Overfed

300-600 Spreader

pulverized combustion unitand oxygen availability in levels from pulverized firsmall, comparably fired utindustrial boiler NOx emissunlike many coal-fired util boiler capacity for different for comparison purposes.	the primary red boilers a lity boilers sions on boilers	are within the size or of the size o	ne ranges of e However, the capacity is ve aseline NOx em	miss depe ry w issi
Although industrial boiler utility boilers, considering emissions from the industrial in meeting air quality star coal use and annual NOx emility should be noted that stong dustrial boiler NOx emission of their large population and starting the starting of the starting population and starting the starting population and starting population	ial category idards. An a issions by bo bker units re ons, in spite and fuel use.	r emission le are signific appreciation oiler type ca epresent appre of their lo	eant and canno for the indus in be gained for coximately 80% www emission le	t be tria rom of
Table 2. Est	imates of Co	na use au uu n	OV THITTOTOTIO	
Table 2. Est From Indu		rtube Boilers		
	strial Water	rtube Boilers	for 1972 NOx Em	issi
	strial Water	rtube Boilers age	for 1972	
Pulverized Fired Tangential Horizontally Opposed Single Wall Vertical	Coal Usa 10 ¹² Btu/Y 80.0 28.8 52.8 5.3	age 4.8 1.7 3.2 0.3	NOX Em. 10 ³ TPy 30 12 21 2	
Pulverized Fired Tangential Horizontally Opposed Single Wall Vertical Cyclone	Coal Usa 10 ¹² Btu/Y 80.0 28.8 52.8 5.3 35.0	age //r % 4.8 1.7 3.2 0.3 2.1	NOX Em: 10 ³ TPy 30 12 21 2 28	Ž.
Pulverized Fired Tangential Horizontally Opposed Single Wall Vertical	Coal Usa 10 ¹² Btu/Y 80.0 28.8 52.8 5.3	age //r % 4.8 1.7 3.2 0.3 2.1	NOX Em. 10 ³ TPy 30 12 21 2	
Pulverized Fired Tangential Horizontally Opposed Single Wall Vertical Cyclone (Subtotal)	Coal Usa 10 12 Btu/Y 80.0 28.8 52.8 5.3 35.0 (201.9) 641.2 567.7 169.6	rtube Boilers age /r % 4.8 1.7 3.2 0.3 2.1 (12.1) 38.3 34.0 10.1	NOx Em. 10 ³ TPy 30 12 21 2 28 (93)	(1 3 2
Pulverized Fired Tangential Horizontally Opposed Single Wall Vertical Cyclone (Subtotal) Stoker Fired Spreader Underfed Overfed	Coal Usa 10 12 Btu/Y 80.0 28.8 52.8 5.3 35.0 (201.9) 641.2 567.7	rtube Boilers age /r % 4.8 1.7 3.2 0.3 2.1 (12.1)	NOx Em. 10 ³ TPy 30 12 21 2 28 (93)	Ž.

to suspension-fired units. The variations in and among stokers and pulverized combustion units is due to the differences in combustion

Combustion modifications including low excess air and staged combusti

4. COMBUSTION MODIFICATIONS TO REDUCE NOx EMISSIONS

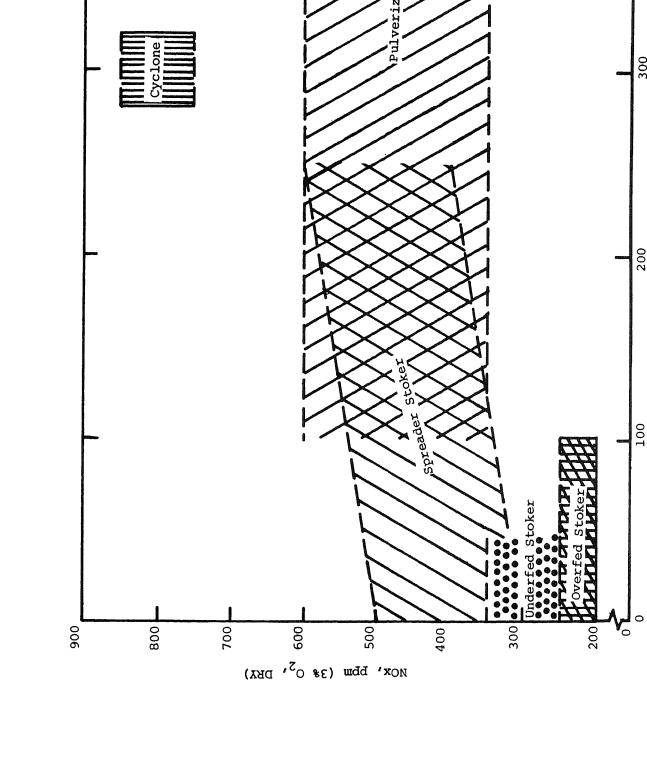


Table 3. Summary of Non-

LEA

5%

5 to 10%

Firing Type

Suspension Firing

Cyclone

Single Wall

Air

BOOS

30 to 45%

Register

Adjustment

15%

Simulated

Injection

Systems

Tangential	10%	-	40%	-
Stokers				
Underfed	10%	NA	NA	-
Overfed	10%	NA	NA	0 to 20%
Spreader	10 to 15%	NA	NA	0 to 5% 10
NA - Not applicable	e			
Low excess air (LE of overall excess a factory boiler open above practical smoment limitations, open presented in Table In many instances, larger available matechniques. For specific presented in the second presented in th	A) involves operair. Minimum exprating conditions tend to be operated by the conditions of the actual reduction of the actual	ccess air as with e rated at co improperance neg ne-percen action po O2) was conits, a	various le er air or flect, etc. t reduction tential of greater that reduction in reduction in tention in reduction in tention in te	e determined by arbon carryover evels (0 to 5% C fuel distribution in excess 0 LEA (considering an the more compin excess air considers and the more compin excess air considers are considers.
a significant reduce the most effective	NOx control met	hod on ex	xisting sto	oker units.
Staging the combust regions can be achi air (OFA) operation emissions by reducizones. The application of the combust of the former of the form	leved through bu These techni ing the availabi ation and reduct	rner-out- ques are lity of c ion poter	of-service very effect oxygen in the still of the	e (BOOS) and over ctive in reducing the primary comb

BOOS is implemented on pulverized coal-fired units by terminating the flow of coal to selected burners (and thereby increasing coal flow to maining burners) while maintaining air flow through all burners. ner, sufficient segregation of fuel-rich and air-rich zones are crea

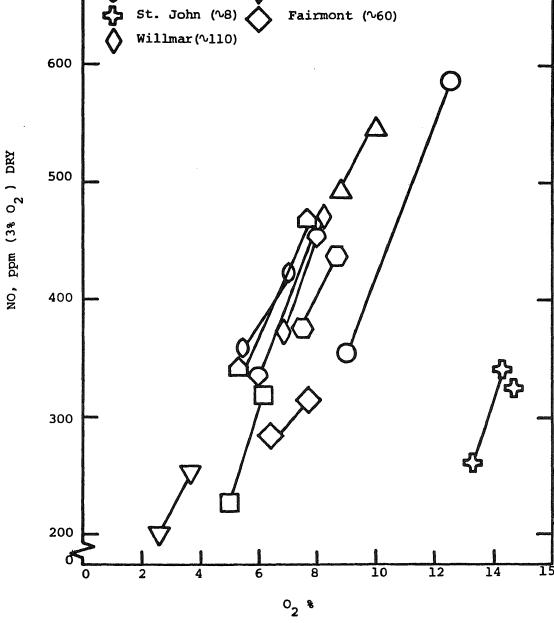


Figure 2. Effect of excess O₂ on NO emissions, spreader stoker units (Numbers in parentheses indicate operating load in thousand pounds of steam per hour.)

coal units. These reduction potentials are comparable to the result utility sized units with the same degree of staging (Ref. 1). The w application of BOOS to industrial units is questionable due to load tions unless modifications to burner and coal preparation systems ar OFA operation has been simulated on stoker units using both existing overfire air injection systems (installed for increased turbulence i volatile combustion regions directly above the bed) and through the systems for auxiliary, wall mounted burners. As given in Table 3, t overfire air injection systems has shown to have little effect on re-NOx emissions and in fact, increased emissions on an overfed stoker. auxiliary burners, however, reduced NOx emission levels by 10 to 20% data indicate that optimum design of OFA ports for NOx control could significant reduction potentials on stoker units. Although data on industrial sized suspension fired unit equipped with OFA ports were able, the results from utility boiler tests showed reduction potenti 15% and 30% for single wall and tangentially fired units, respective The data presented in this paper were compiled from field test programs conducted by KVB under sponsorship of the EPA and DOE (Refs. 3 For the most part, the reduction potentials presented in Table 2 per

the degree of staging (percent of BOOS) which is severely limited on sized units by the few burners involved. Reduction potentials prese Table 3 represent operation with 25% of the BOOS and reduced loads. indicates the typical NOx reductions achieved on single wall-fired p

or reduced load conditions over extended periods must be made prior full implementation as routine operating procedures. It should also be emphasized that there are large unit-to-unit varia

conditions at one load point for short duration tests under steady o conditions. Examination of these combustion modifications under flu

tions in coal-fired industrial boiler NOx emissions, even within the boiler design type. This is due to varied boiler geometry with size and coal type. Boiler operating practice, maintenance, coal preparaand coal combustion characteristics often vary from plant to plant ev within the same region. Frequently a plant in the northeastern U.S. obtain coal simultaneously from two or three sources. Therefore, it unusual to see baseline NO $\mathbf x$ emissions very by as much as 400 ppm for boiler type. Because of this wide variation in baseline emissions, t

type, etc.

is cautioned that the NOx reduction potentials discussed previously o be guaranteed for all existing units regardless of boiler age, design

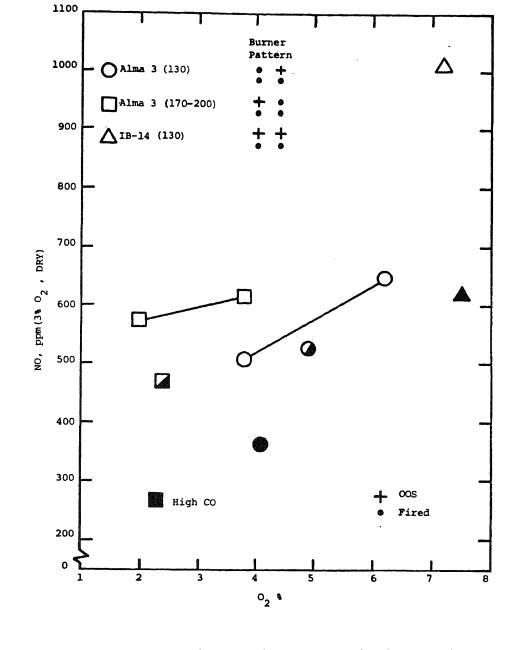


Figure 3. BOOS operation on single wall-fired pulverized coa units for all burners in service (open symbol); no air to BOOS (half shaded symbol); and normal air distribution to the BOOS (completely shaded symbol (Numbers in parentheses indicate operating load in thousand pounds of steam per hour.)

owners and operators. Although the implementation of staging technique industrial units has been applied only on a test basis, experiences (1) utility units using BOOS and OFA as normal operating procedures industrial units operating with LEA for efficiency reasons can give into their possible initial and long term impacts. Some of the more important concerns and conclusions drawn from a br ment of operational considerations are listed below: The improper application of LEA or staged combustion can result in local reducing conditions that lead to water wall corrosion. This potential problem is being extensively studied on utility boilers by EPA but very little industrial boiler work has been performed.

. Low NOx emissions require careful attention to boiler maintenance and repair, particularly with regard to burners, combustion controls, and other fuel/air equipment.

The impact on boiler operations of the initial and long-term use or tion modifications is, in many respects, as important as the associ NOx reduction potential when considering the use of these technique cation of procedures that would seriously affect the safety, relia expected life time of these units would be considered unacceptable

- . Improved combustion controls and oxygen analyzers may be required to maintain optimum low NOx operating conditions . Proper implementation of low-NOx boiler operating modes
 - need not necessarily lead to increased fuel use or reduced operating efficiency. In most cases, the improved excess air control offsets the effects of delayed combustion resulting in acceptable CO and particulate emissions at design efficiency.

sponsorship, NOx emission levels under 100 ppm have been accomplished

- . LEA can generally be implemented with a net savings in fuel use whereas advanced staging requires hardware and auxiliary equipment at 0.1 to 0.3% of the total annual cost of operation.

6. ADVANCED CONCEPTS FOR NOx CONTROL FROM COAL-FIRED INDUSTRIAL BOILERS

Advanced staged combustion low-NOx burner/boiler concepts currently developed (Refs. 7,8) for utility boilers have the most promise for pulverized coal industrial boilers. Under government and utility in Advanced NOx control concepts for stokers revolve around the use of overfire air coupled with good undergrate air management to reduce the obed excess air and to lower NOx emissions. Extensive research into cont NOx emissions from stokers have not been funded but a yet-to-be-awarded EPA program to examine stoker emissions control design options is expect to emphasize NOx control.

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Industrial and Utility Boilers," presented at Second Station

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SUMMARY

The "Low NOx Heavy Fuel Combustor Concept Program" is a part of t DOE/LeRC "Advanced Cogeneration Technology Project" (ACT). The program is a contract effort with total funding provided by the Department of Energy, and technical program management provided h Main program objectives are to generate and demonstra the technology required to develop durable gas turbine combustors for utility and industrial applications, which are capable of sustained, environmentally acceptable operation with minimally processed petroleum residual fuels. The program will focus on "dry" reductions of oxides of nitrogen $(NO_{\mathbf{x}})$, improved combustor durability and satisfactory combustion of minimally petroleum residual fuels. Other technology advancements sought include: fuel flexibility for operation with petroleum distillates, blends of petroleum distillates and residual fuels, and synfuels (fuel oils derived from coal or shale); acceptable exhaust emissions of carbon monoxide, unburned hydrocarbons, sulfur oxides and smoke; and retrofit capability to existing engines. of these capabilities will be accomplished with a minimum and acceptable sacrifice in other combustor performance requirements. Program goals are intended to be optimistic projections of attainable emission reduction and fuel flexibility. The intent is to generate advanced combustor design technology rather than to verify already available technology. Further, it is intended that the generated technology be retrofittable into existing engines in the near-term. The technology generated will be primarily applicable to near-term industrial and utility engines with pressure ratios of 10:1 or higher, which are suitable for cogeneration applications. The technology will also be applicable

INTRODUCTION

to future engines.

This paper describes the Low NO_{X} Heavy Fuel Combustor Concept Program including its objectives, program plan, schedule, the basis for its emphasis on heavy oil and synfuels, pollution and performance goals, program approaches to pollution reduction, and statuto date.

Limited near and mid-term fuel supplies, as well as competition from other users of natural gas, light and mid-distillates could make it attractive for utility and industrial gas turbine manufacturers and users to fire residual oils in their gas turbine

emission standards. Oxides of nitrogen emission standards are difficult to meet with current light distillate fuel oils, and will become more difficult with residual oils and synfuels. Water or steam injection has been successful in some installat to reduce thermal NO_x formation. However, this approach is cl not a universally acceptable method since it involves consider additional installation and operational costs, and does not re-NO_x from fuel bound nitrogen. Smoke will also increase with he

local environmental regulations.

represents a still more difficult challenge due to their antiincrease in impurity content, lower hydrogen-carbon ratio and levels of fuel bound nitrogen. Also, under limited circumstan stationary gas turbines may be required to produce ultra-low emissions using presently available clean fuels due to stringe

Exhaust emissions from future gas turbines must also meet Fede

It appears that substantial reduction of pollutants can be atta The concepts for pollution reduction now exist. However, although the mechanisms of pollution production as well as techniques for reducing pollutants are generally known, application of these techniques to specific combustor-engine designs has not yet

fuel firing as a result of lower fuel hydrogen content.

is needed to apply these concepts. The Low $NO_{\mathbf{x}}$ Heavy Fuel Comb Concept Program was initiated to provide a timely evolution of combustors. The program aim is to develop this required pollution reduction technology, apply the technology to combustors for industrial a utility applications, solve interface and performance problems which low pollutant combustor designs create for engine install tion, and demonstrate the pollution reductions in steady state

demonstrated the anticipated pollutant reductions without compromising other combustor parameters. Thus additional technological

and transient testing of development engines. PROGRAM DESCRIPTION

by the NASA Lewis Research Center. The program's primary objec

General

The Low ${
m NO}_{
m X}$ Heavy Fuel Combustor Concept Program is a multi-yea contract effort funded by the Department of Energy and administ

are the following:

- fuels and natural gas in the near term.
- 4. To permit transition to synthetic liquid fuels when they become available.
- 5. To investigate and develop the technology required to achieve ultra-low emissions (one-half the EPA $\rm NO_X$ standard) with current clean distillate fuels.
- 6. To demonstrate the derived technology in full-scale engines.

The program is primarily applicable to near-term industrial and utility engines suitable for cogeneration applications. Additional applicability is desired for future, higher pressure ratio engines

Program Plan

It is anticipated that the program will be conducted in three phases. An overall program diagram is contained in Figure 1. Program phases are discussed below:

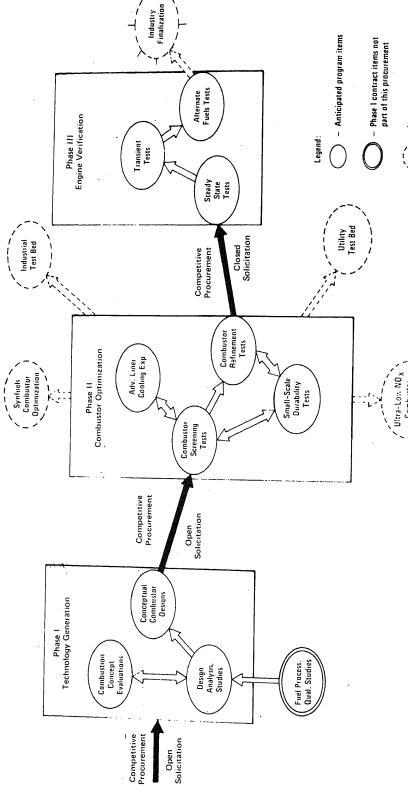
Phase I - Combustion Technology Generation

This phase, which is currently in the process of being implemented consists of combustion studies, fuel studies, development of combustion designs, tests, and retests of multiple combustion concepts to determine the best concepts for achieving program objectives. The specific objective of Phase I is to generate the emission reduction and fuels technology required for future program phases. This phase, with the exception of the brief descriptions of Phases II and III presented directly below, is the subject matter of this paper. As with all program phases, Phase I will be a contract effort. Multiple contractors are anticipated.

Phase II - Combustor Screening and Optimization

This phase will consist of incorporating the Phase I combustion results into engine-combustor hardware, component testing of promising combustor concepts, iterative redesign and retest of multiple combustor design approaches to determine the best combustor approaches for achieving program goals, and development of combustor liner designs suitable for heavy fuel utilization. The most promising combustor designs will then be tested further to develop the required overall performance, durability and engine adaptability required for engine utilization. Eligible contractor for this phase will not be restricted to those contractors

Low NO_X Heavy Fuel Combustor Program



Phase III - Engine Verification

This phase will consist of evaluating the best combustor(s) of Phase II as part of a complete engine. The intent is to demonst in short duration engine testing the emission reductions achieve fuel flexibility and performance at steady-state and transient conditions. Contractors for this phase will be restricted to

those contractors successfully completing the Phase II effort. One or more contractors are visualized. Since the program emphasizes utilization of minimally processed heavy petroleum fuels, and since burning of petroleum distillate distillate residual blends and synfuels will be assessed but no optimized, the possibility exists for additional program efforts

regarding these latter fuels, which are not a part of the curren program. Also, if feasible, additional program efforts involvin installation of the derived combustors in field engines for extended evaluation may be undertaken. These potential efforts are contained in dashed lines in Figure 1. Program Schedule

The planned program schedule is shown in Figure 2. Phase I efforts were initiated in September 1978 with issuance of NASA RFP No. 3-870802. Contract signings are anticipated to occur prior to January 1979, with completion of this phase scheduled to occur within 16 months of contract signing. An approximate 6 month delay is anticipated between the completion of Phase I and the initiation of Phase II, due to procurement

procedures. Phase II will be approximately 30 months in duratio It is anticipated that Phase III will be initiated immediately upon completion of Phase II. Phase III will be approximately 16 months in duration.

Fuels Considerations

Fuels availability

Limited near and mid-term petroleum fuel supplies, as well as competition from other users of scarce fuels, could make it

attractive for utility and industrial gas turbine manufacturers and users to fire residual oils in their gas turbine equipment. Also, the national goal of reducing dependence on foreign energy

supplies in the far-term will make it necessary to use synfuels

made from abundant national supplies (Figure 3) of coal and oil shale. Figure 3 also shows the hydrogen to carbon atomic ratio of the various fuel sources. This ratio will be shown in later sections of the paper, to be a major consideration in gas turbin

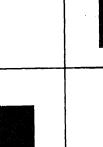
combustor designs. Figure 4 shows the similarity of a heavy

a a series de la contrada li c

84 83 Proposed Program Schedule CX α 7 ζ/ Description

70	
0	
0 _	
2	
2	

Phase I:









Phase III:

Phase II:



Figure 3

U.S. Remaining Fuel Resources (Approximate)

H/C Ratio	2.00
1015 BTU	200
	etroleum

Synthetic Fuels*

1.75	1.90	0.75
100	20,000	90,000
Tar Sands	Oil Shale	Coal

Liquid Fuel Consumption US 40 x 1015 BTU/Year

^{*}Fossil Fuels Derived from Other than Petroleum

	Fired Engines	
Figure 4	Directly Fin	
	d Fuels for	
	Liquid	

	Engines
	Fired
Figure 4	Directly
	for
	Fuels
	75

	Engines
	Fired
Figure 4	Directly
	9
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Engines
Fired
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Mid-Term Minimally Processed Coal De

*H-Coal

I-Ligh Dist'te

Resid.

Dist'te.

Dist'te.

Solvent Donor

Residuals

=2 Distillate

Key Characteristics

*Exxon

Heavy Petroleum Near-Term

Todays Std.

Heavy

*Light

1.5

1.3

1.01

0.42

7

.05 to .5

90:

Nitrogen (Wt. %)

Fuel Bound

 ∞

1.01

1.38

1.09

1.3

2,0

Hydrogen/Carbon

(Atomic Ratio)

Ash (Wt. %)

0.2

0.2

Ē

Ē

.03

.05

0.8

0.48

0.22

0.18

9.0

0.5 to 2.7

0.5

Sulfur (Wt. %)

gines	
E E	
Fired	
>	

reasibility of synthess. To be economically competitive, synthetic liquids must be minimally processed, i.e., hydrogenation of coal-derived crudes must be kept to an absolute minimum. Phase I Test Fuels

the EPA standard are in effect.

Three test fuels have been specified for Phase I. These fuels are described in Table I. Fuel A is a petroleum distillate simulating Diesel #2 properties. The objective of testing with this fuel will be to achieve ultra-low $\mathtt{NO}_{\mathbf{X}}$ which is defined as one half the applicable EPA standard. Ultra-low $NO_{\mathbf{X}}$ combustors are

Fuel B is a petroleum residual fuel and is the major basis for combustion design in this program. Correspondingly, test efforts will emphasize utilization of this fuel. Fuel C is also a petroleum residual, with degraded properties as indicated by the reduced hydrogen-carbon ratio. The intent of testing with this fuel is to simulate operation with synfuels derived from coal or shale. It is anticipated that if available in sufficient quantity, synfuels will be substituted for fuel C during the program.

required in areas where local regulation, more stringent than

fuel tests will also be conducted in Phase I. Test fuels B and C will be doped with pyridine to investigate combustion approaches for reducing fuel bound nitrogen conversion. Levels up to 0.5% by weight of fuel bound nitrogen will be investigated with fuel B. Levels up to 1.2% by weight of fuel bound nitrogen will be investigated with fuel C.

In addition to testing with the fuels defined above, additional

In addition, blends of fuel A with fuel B, and blends of fuel A with fuel C will also be investigated. The objectives of these tests are: to determine the tradeoffs concerning fuel quality and its effects on combustor emissions and performance.

Several of the difficulties anticipated to be encountered in

burning minimally processed heavy fuels are listed in Table II. Increased alkali metal content of heavy fuels are anticipated to create corrosion and deposition problems on combustor liners

and turbine blades. Increases in boiling range increase tendencies of qum formation and carbon deposition on fuel

nozzles and combustor liners. Reduced hydrogen content causes increased radiation during combustion, thus producing increased heat loading to combustor liners and adversely affecting combustor

COMPOSITION:			
	NMR	12.8 0.2	10.840.2
HYDROGEN, WT. %	ASTM D129	0.8 max.	0.8 max
SULFUR TOTAL, WT. %	Kjeldahl	0.1 max.	0.2 max
*NITROGEN TOTAL, WT. %	OCMS	REPORT	REPORT
HYDROCARBON COMPOSITIONAL ANAL.	ASTM D482	20 ppm max.	0.04 max
ASH, WI. %		REPORT	REPORT
ASH MELT TEMPERATURE, OF	TBD	KBIOKA	
AROMATICS TYPE:	4 cm 4 p 1 2 1 0	REPORT	REPORT
AROMATICS TOTAL, VOL. %	ASTM D1319		REPORT
SATURATES	TBD	REPORT	
OLEFINS	TBD	REPORT	REPORT
NAPHTHALENES	TBD	REPORT	REPORT
CARBON RESIDUE:			
ON 10% WI., %	ASTM D524	REPORT	REPORT
	11	REPORT	REPORT
ON 100% WT., %	TBD	REPORT	REPORT
WATER & SEDIMENT, VOL. %			
VOLATILITY: DISTILLATION TEMPERATURE, VOLUME			
DECOMEDED OF may-			
RECOVERED, OF max.	ASTM D86	REPORT	REPORT
INITIAL BOILING POINT	MOTH DOO	425 <u>*</u> 25	600 ± 50
10%	"		-
50%		REPORT	REPORT
FINAL BOILING POINT	11	650 \$ 50	1000 100
RESIDUE		REPORT	REPORT
FLASH POINT, OF	ASTM D93	REPORT	REPORT
GRAVITY, OAPI	ASTM D287	REPORT	REPORT
FLUIDITY:			
POUR POINT, OF	ASTM D97	20 max.	50 max.
VISCUSITY AT 100 OF:			
	ACTM DAGE	REPORT	DEDINOT
KINEMATIC, cS	ASTM D445		REPORT
SAYBOLT UNIVERSAL, SEC.	ASTM D88	REPORT	REPORT
COMMUSTION:			
NET HEAT OF COMBUSTION, BTU/LB	ASTM D2382	REPORT	REPORT
THERMAL STABILITY:			
JETOT, BREAKPOINT TEMPERATURE, OF			
(TDR, 13; △P, 25 mm)	ASTM D3241	REPORT	REPORT
TRACE METAL ANALYSIS: ppm		Total	
V	TBD	REPORT	REPORT
Ni	100		
Na.	"	REPORT	REPORT
		REPORT	REPORT
K.	91	REPORT	REPORT
Mg	61	REPORT	REPORT
Ca	n	REPORT	REPORT
Pb	11	REPORT	REPORT
Cu	41	REPORT	REPURT
_	91	REPORT	REPORT
Fe	11	_	
re Si		REPORT	REPORT
	•	REPURCT	REPORT
Si Zn		REPORT	
Si Zn Ba	**	REPORT	REPORT
Si Zn Ba Mn	11 11		
Si Zn Ba	**	REPORT	REPORT

Fuel Considerations & Impacts

		Fuel Types		
Parameter	Current # 2	Heavy Oils	Current # 2 Heavy Oils High F.B. Nitrogen	Effect
Alkali Metal Content	Low	High	Higher	Corrosion & Deposition
Typical Boiling Range ⁰ R	380-650	600-1000	600-1000	Gumming & Carbon Formation
Hydrogen Content Wt. %	12.2-13.2	10-12.5	9-12.5	Luminosity + Smoke
Thermal NO _X	High for All in Relation to Stds.	in Relation	to Stds.	
F.B. Nitrogen	0-0.2	0-0.5	0 1 2	× ON

Conversion

0.5-1.2

0-0.5

0-0.2

% Wt.

Emission Goals

F.R. 40 CFR Part 60 and are subject to all of the constraints and corrections contained in this citation. The emission goals are contained in Table III. Engine operating conditions for which the goals apply are discussed in a subseque section. These operating conditions incorporate all engine

Program emission goals are based on EPA Proposed Regulation,

power levels for load following engine-combustors. The sulfur dioxide goal represents a limitation on fuel sulfur, since all of the fuel sulfur is transmitted through the combustor. It is included here for consistency with the referenced citation. Subsequent program phases will address the

question of fuel sulfur level regarding its removal either upstream or downstream of the combustor. Smoke is not currently regulated by the EPA. Rather, it is subject to local regulation. An S.A.E. number of 20 is consistent with advanced state-of-the-a combustor design practices.

Achievement of the Oxides of nitrogen (NO_x) standard represents the most difficult program goal for achievement. Water or steam injection to reduce oxides of nitrogen by reducing flame temperatures will not be relied upon as a control device in

this program. "Dry" reductions of oxide of nitrogen through combustor design will be sought. At present, the technology required to control of NO_X through combustor design is not available, even with clean distillate fuels. The current NO, emissions will have to be reduced by a factor of 2 to 3 to meet goals shown in Table III. There are also indications that achieve with heavy fuels. This is shown in Figure 5.

achievement of the NOx standard value will be more difficult to Fuel bound nitrogen levels in the fuel also make achievement of the $\mathtt{NO}_{\mathbf{X}}$ standard more difficult. Current EPA regulations permit correction for fuel bound nitrogen up to 0.25%. Fuel bound

nitrogen levels in excess of 0.25% must be compensated for by reducing the conversion of fuel nitrogen into \mathtt{NO}_{X} . Typical fuel bound nitrogen conversion data, for a current production industria engine are shown in Figure 6.

It is anticipated that additional emission goals will be added to future program phases. For example, a particulate goal is anticipated for program Phases II and III.

Emission Goals 900

Pollutant

Maximum Level

Operating Cond.

E

:

S.A.E. Number = 20

Smoke³

Oxides of Nitrogen¹

75 PPM @ 15% 0²

150 PPM @ 15% 0² Sulfur Dioxide^{1.2}

Notes:

EPA Proposed Regulation, F.R. 40 CFR Part 60

1,2 - Limit of Fuel Sulfur Content

3 - No EPA Regulation, Local Rules

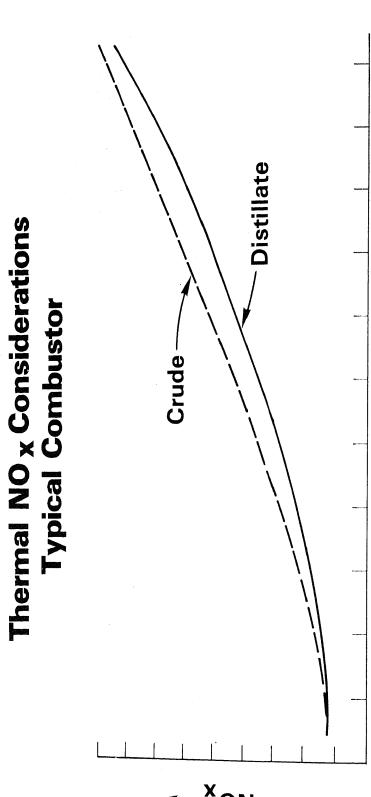


Figure 5

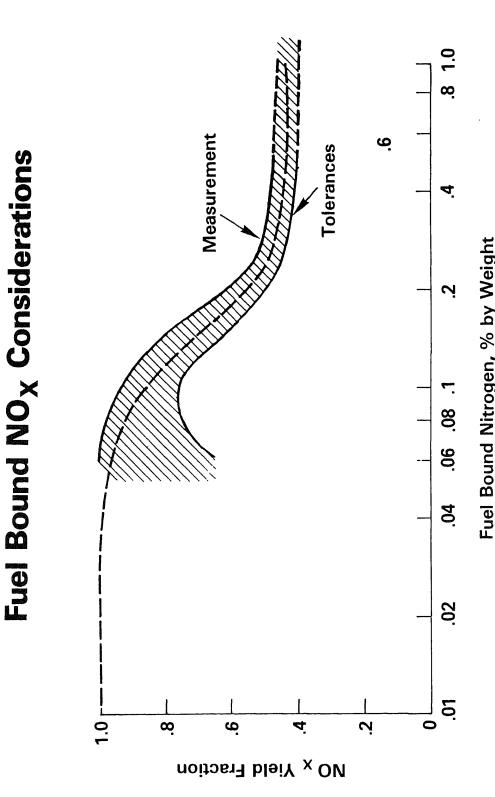


Figure 6

The combustion efficiency goal effectively imposes maximum allowable levels of unburned hydrocarbon (HC) and carbon monox

(CO), since levels of these emissions are directty relatable t

combustion inefficiency. Conversely, program measurements of

combustion efficiency are specified to be recorded through emission level determinations. Current combustors operate ver

Test Conditions Combustor test conditions over which the emission and performa

pressure and fuel/air ratio.

Combustor Considerations and Design

efficiently at high engine power points (50% of engine rated power level and above). However at lower engine power levels, especially at spinning idle conditions, combustion inefficience occur with most current engines.

goals apply are contained in Table V. Implicit in the selecti of these test conditions is a requirement for load following capability. Load following capabilities are deemed to be necessary for this program because cogeneration applications for the derived technology are visualized. Most industrial and utility gas turbine engine combustors operate efficiently at a nominal base load condition and somewhat less efficiently at off-design or lower power conditions. The requirement that . engine combustors operate efficiently over a load range is a significant requirement. To achieve this type of operation, combustor performance must be optimized for a variety of

combustor inlet conditions, including those of low temperature

Advanced combustor designs will be emphasized in the Phase I program. A non-inclusive list of pollution reduction technique which will be investigated in the program are contained in Table VI. Included in the table is the pollutant of concern

Control of thermal $\mathrm{NO}_{\mathbf{X}}$ involves reduction of flame temperatures below 3000^{OF} and short residence times of combustion gases at high temperatures. Simultaneous control of thermal $\mathtt{NO}_{\mathbf{v}}$ and \mathtt{smo} additionally requires uniform distribution of fuel and air, and

avoidance of excessively high fuel rich zones. Control of the conversion of fuel bound nitrogen into $\mathrm{NO}_{\mathbf{X}}$ involves burning und fuel rich conditions or, correspondingly, oxygen lean condition

The technology developed in Phase I should be applicable to all types of gas turbine combustors. An illustration of these

and the corresponding pollution reduction concept.

Table IV Performance Goals

Combustion Efficiency*

99% at All Operating Conditions

Total Pressure Loss Outlet Temperature Pattern Factor

V

11

6% at Base Power Load

0.25 at Base Load & Peak Load Power

Pattern Factor Combustor Exit Radial Temperature Profile

Equivalent to Production Comb. Values

||

^{*}Calculated on a Deficit Basis from Measurements of Co, THC & Co2

Proposed Combustor Test Conditions

Cold Start
Spinning Idle
30% Rated Power

50% Rated Power 70% Rated Power

80% Rated Power - Nominal Base Load Condition \$00% Rated Power - Peak Load Condition Parametric Variation

N Sign

Pouton Reduction echniques	Reduction Concept	ion Diluent Injection into Burning Zone Quick Quench Catalytic Combustion	Premixed/Prevaporized Burning	Ultra Lean Burning	Advanced Fuel Injection	Multiple Fuel Utilization
	Pollutant	Thermal NO x Reduction	Thermal NO x and	Smoke Reduction		

AC 79-0522M 5-14

Rich Burning with Controlled Quench

Organic NO x Conversion

Reduction

Multi-zone combustors represent advanced technology which is currently being evolved for both ground based and aircraft gas turbine combustors. Multi-zone designs, while considerable more complex than current designs, provide additional degrees flexibility in staging fuel and combustion to optimize perform a variety of test fuels, emission and performance constrates.

CONCLUDING REMARKS

It is anticipated that Phase I of this program will provide t technology base for future program phases. Specifically it i

1. Definition of the most promising combustor design approaches for utilizing heavy fuels derived from petroleum a other sources.

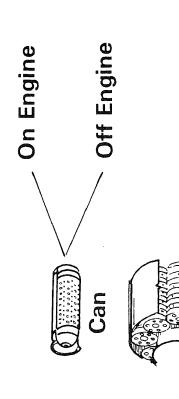
anticipated that Phase I will provide the following:

- 2. Definition of tradeoffs involving fuel quality and combustion and emission performance.
 - 3. Identification of realistic fuels for future progra
- phases.

 4. Identification of engine applications for the derimentation of conceptual engine technology. This will include preparation of conceptual engineers.
- technology. This will include preparation of conceptual engicombustor designs.

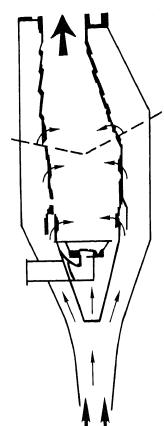
 5. Identification of development efforts required to
- utilize minimally processed heavy fuels in sub-component combustor areas such as fuel systems, liners, etc.

Potential Combustor Types Figure 7

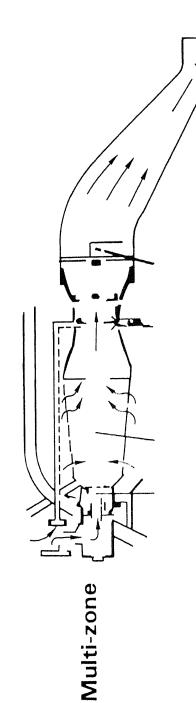


Can-Annular
Annular

Combustor Designs



Single-stage



verger

Midwest Research Institute 425 Volker Boulevard Kansas City, Missouri 64110

ABSTRACT

Midwest Research Institute conducted a project under contra

with Argonne National Laboratory to assess the economic and energy pacts of particulate control systems in coal-fired power plants. The assessment was based on major functional variables such as plant size (100 to 1,000 MWe), location, coal type, and emission standards. The work resulted in the generation of algorithms to predict equipment cost, installation costs, and energy usage for various particulate of the trol devices. The devices considered were: electrostatic precipitations (hot-side and cold-side); fabric filters (reverse air and shake types); and wet scrubbers.

A boiler performance model was developed using variables as plant size, coal characteristics, etc. The output from this mode (i.e., flue gas flow rate, grain loading, etc.) was utilized in condevice performance models to generate required design and operating parameters for the control systems under study. The design and opening parameters were then used in the cost models that were also developed in this program.

The cost models aggregate three cost items: (a) the first costs (capital investment); (b) total first-year annualized costs; a (c) the integrated cost of ownership and operation of the control equipment over an assumed plant lifetime of 30 years. The models have been programmed for speedy computation. However, the algorithms are easily solvable with a hand calculator. In addition, suitable guide line values have been provided for independent variables wherever neessary. Case studies are presented to demonstrate results of the models.

0.03 1b/10° Btu). Since there are a name of a need for being able available for particulate control, there is a need for being able estimate the economic and energy impacts of each control option for given set of plant specifications. Realizing this need, Argonne tional Laboratory contracted with Midwest Research Institute (MRI develop the necessary algorithms to predict equipment cost, instation costs, and energy usage for five particulate control devices electrostatic precipitators (ESPs) including hot-side and cold-side fabric filters, both reverse air and shaker type, and wet scrubber

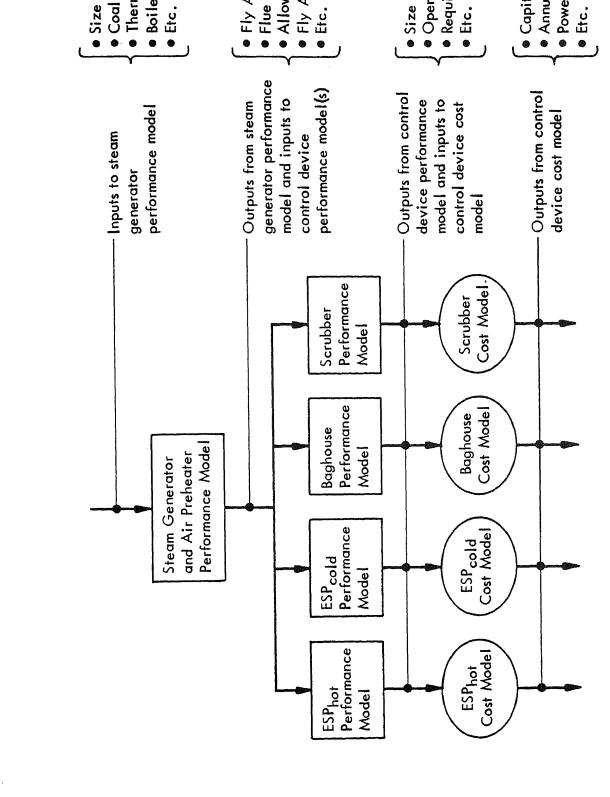
of a boiler that relate to the design of fly ash control equipmen This boiler performance model utilizes input values such as plant coal characteristics, and boiler type for the computation of para critical to control devices (e.g., flue gas flow rate, uncontroll particulate emissions, etc.). Thereafter, algorithms were develo that use the information generated by the boiler performance mode plus the emission limit specified, to compute various control dev design parameters (e.g., collecting area for an ESP). A subseque of algorithms use these device parameters to compute equipment an erating costs and energy usage. The breakdown of cost items cons is presented in Figure 2. The cost and performance algorithms di

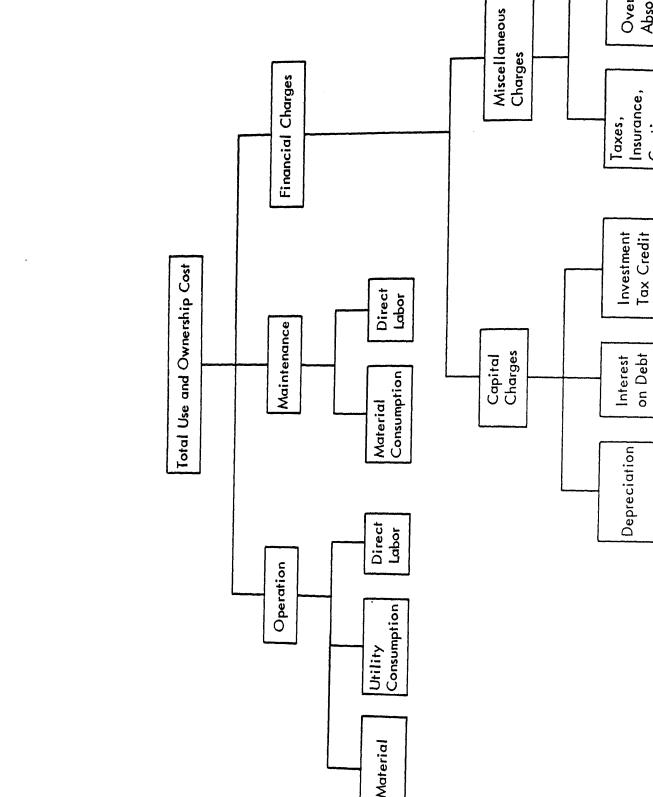
cussed in this paper are composites of relationships published in literature and additional information obtained as part of this pr

in Figure 1. A set of algorithms was developed to quantify the a

The methodology used for the model development is prese

The following sections of this paper describe the salie features of the boiler performance model as well as the control d performance and cost models, including the various cost and energ sumption factors that were considered. The final section present summary of the results obtained from these models when applied to hypothetical 500-MWe plant at three different geographic location burning three different coals.





suggested default values are given. Inis procedure is also followed for many of the other algorithms developed in this project.

Table 1. Steam Generator Performance Model Inputs

Default

700

350

0.85

0.65

0.10

0.20

0.15

٩r

lb fly ash/lb

of ash in coal

		2010-
Description	Unit	Value
Generation rate	MWe	-
Boiler type Pulverized coal dry bottom or wet bottom, or cyclone	-	-
Plant location, state	•	•
Heating value of coal	Btu/lb	æs
Plant thermal efficiency, decimal fraction	-	0.388

Heating value of coal
Plant thermal efficiency, decimal fraction
Flue gas temperature

For pulverized coal dry bottom boiler

For pulverized coal wet bottom boiler

Excess combustion air, decimal fraction

Coal analysis, decimal fraction for N, C,

For pulverized coal boilers

At preheater inlet At preheater outlet

Boiler emission factor

For cyclone boiler

For cyclone boilers

H, S, and H_20

- Flue gas flow rate, acfm,

. Coal firing rate, tons/hr,

- . Heat input rate, 106 Btu/hr.
- . Mean diameter and standard deviation of fly ash parti size distribution, and
- . SO₂ flow rate in flue gas, lb/min.

The above parameters then constitute the inputs to the v

an individual basis, several aspects that the models have in commo

identified.

allows for state-to-state variations in costs, including wage rate

control device design models.

Before describing the control device design and cost mod

First, the algorithms generate costs in 1978 dollars, bu provisions have been made for the user to modify the costs to any dollars beyond 1978 by using projected cost indices.

Second, a table is provided in the original report $\frac{1}{2}$ tha

power costs, construction costs, and land acquisition costs. In the cost models, which may be adjusted for different locations, an ave wage of \$7.41/hr was used for utility workers and an average land of of \$10,000/acre.

Third, the cost of the control devices was amortized on a accelerated basis over a 5-year period, per the Tax Reform Act of Interest was assumed to be 8%, based on the prime rate, but the use may specify other values. Also, an investment tax credit of 10% was applied for the first year of operation.

Fourth, one of the cost criteria used in the overall ecor analysis was the total cost of owning and operating the plant over specified plant lifetime (e.g., 30 years) in terms of first-year do This computation requires several economic projection figure including discount rates for present value analysis and increases i

The performance and cost models developed for each control device contain several algorithms. The following sections discuss th more important ones and their development.

A. Cold-Side ESP

. Type of boiler. . Current density, . Power density,

. Voltage,

ter for the ESP cost model.

tion costs:

Performance model: The familiar Deutsch equation was

used for "sizing" a cold ESP. This equation requires knowing the par

ticle migration velocity, so a modified form of algorithm developed b

tion velocity parameter as a function of:

Southern Research Institute $(SRI)^{2/}$ was used which computes the migra

. Number of electrical sets,

. Moisture content of flue gas, . Sulfur and ash in coal,

. Flue gas temperature, and

. Uncontrolled fly ash loading.

Since all of the above variables may not be known by the us

suggested default values are given, some of which are selected on the

basis of the sulfur content of the fuel.

the gas flow rate and the required collection efficiency to compute t collecting area. The collecting area then becomes a major input para

The Deutsch equation uses the migration velocity along with

2. Cost model: Equipment and installation costs for the

 $EC_C = 45.94 A_{CP}^{0.88}$

 $IC_C = 23.58 \cdot ACF \cdot A_{CP}^{0.896}$

cold ESP are computed using algorithms developed from a model by Bubenick $\frac{3}{2}$ and data reported by the Industrial Gas Cleaning Institute (IGCI). $\frac{4}{}$ The following equations result for equipment and installa A_{CP} = collecting plate area, ft² ACF = area construction factor

The cost model also contains several other cost algorithms for puting:

- . Ash handling equipment cost,
- Ash handling installation cost,
 - . Land cost,
 - . Electrical capacity charge, . Power cost,
 - . Operating labor cost,
 - . Maintenance material cost, and . Maintenance labor cost.

The electrical capacity charge in the above list rep the cost of additional power plant capacity that is required t the electrical requirements of the control device. The value

ciation and investment tax credit), the cost models also inclu taxes, insurance, and contingency.

used is \$900/kw.

B. Hot-Side ESP

1. <u>Performance model</u>: The hot-side ESP model also the Deutsch equation for computing the collecting plate area.

In addition to the financial charges discussed earli

available data on hot ESP were not sufficient to develop an al for migration velocity, the user must specify a migration velocity.

- select one of the suggested default values, which are as follows 0.30 ft/sec for pulverized coal boiler burning coal > 1% sulfur
 - 0.25 ft/sec for pulverized coal boiler burning coal v < 1% sulfur
 - 0.18 ft/sec for cyclone boiler

TOH - 9.300 ACF AHI

where:

 EC_{H} = hot ESP equipment cost, 1978 dollars

 IC_{H} = hot ESP installation cost, 1978 dollars

 A_{HP} = collecting plate area, ft²

ACF = area construction factor

Algorithms were also developed for other cost items listed above. These algorithms are similar in form to those for the cold ES however, one additional factor included for the hot ESP is heat loss from the ESP due to higher operating temperature. It was assumed that this heat loss results in additional fuel consumption to maintain the power output. Since data collected in this project indicated that the average drop in the flue gas temperature across a hot ESP is about 7° this was the value used in an algorithm to compute the annual cost for the additional fuel. The cost of the fuel is based on a default value of $\$1.75/10^6$ Btu. The annual cost of this heat loss is a significant portion of the total annual operating cost for a hot ESP.

C. <u>Fabric Filters</u>

1. Performance model: Performance and cost models were developed for both reverse flow and shaker type baghouses, the costs based primarily on cloth area required. This parameter is calculated the performance models using an air-to-cloth ratio specified by the user, or a default value of 2.0 $acfm/ft^2$ for reverse flow type and 2 $acfm/ft^2$ for shaker type. These are net values, allowing for one con

The pressure drop through baghouses is considerably higher than in ESPs, and it significantly affects operating costs. Therefor algorithms were developed to compute the pressure drop using information baghouse manufacturers and the recent TVA/Shawnee project. $\frac{5}{}$

partment being off-line for cleaning and one off-line for maintenance

```
ECBB = 10.0 GCV
```

ECSB = equipment cost, shaker baghouse, 1978 dol

Gross cloth area is also the major parameter use

 $RBC_{RR} = 0.78 GCA$

RBC = 0.03 STA

RBCRB = cost of replacement bags, reverse flow ?

RBCSR = cost of replacement bags, shaker baghous

It was assumed in the default condition that all

The algorithms developed for the financial charg

be replaced every 3 years, although the user may specify s Additionally, equations were developed for bag replacement

installation costs for the baghouses. Many of the other e operating costs are similar to the ESP model. But an addi item considered for the baghouses was bag replacement. Av on replacement costs were used to develop the following eq

 $EC_{SB} = 21.08 \text{ GCA}^{0.966}$

where:

ECRB = equipment cost, reverse flow baghouse, 19

GCA = gross cloth area, ft²

1978 dollars

GCA = gross cloth area, ft²

dollars

this cost item:

to those for ESP.

where:

to the absorption of certain amounts of SO_x.) Development of the scrubber performance model was based on work by Calvert 6,7,8 and involves a trial and error procedure to determine the pressure drop and liquid-to-gas ratio required. Several simplifying assumptions were made in developing the design equations. Some of these assumptions relate to the specific application area of the model, viz., fly ash control in coal-fired boilers. Total equipment cost for the venturi scrub Cost model: was derived from costs reported in the literature. Regression analys indicated that these data can best be expressed by: $EC_{s} = 1.59 Q_{s}^{1.062}$ where: EC_S = equipment cost, scrubber, 1978 dollars Q_S = saturated flue gas flow rate, acfm

<u>Performance model</u>: The model developed (for venturi

scrubbers) considers fly ash removal only and excludes those scrubber systems in which particulate and SO, control are achieved simultaneously. (However, it does consider the neutralization requirements du

Several other cost algorithms were developed to determine: Installation cost, Land cost (for the scrubber and for a settling pond),

- . Electrical capacity charge, . Operating labor cost, . Material cost (lime and water),
- . Maintenance material,

. Power usage,

- . Maintenance labor, and . Flue gas reheat cost.

Like the hot ESP heat loss, the flue gas reheat is an addi-

tional cost associated with wet scrubbers. An algorithm was develope to calculate the cost for equivalent fuel. The algorithm assumes an energy cost of \$1.75/10⁶ Btu and a reheat requirement of 50°F, unless the user specifies otherwise.

This model also includes all the financial charges discusse

case studies to derive design and/or size specifications for the control devices based on the models described in the earl (Table 3). Table 4 presents the cost comparisons for the contr resulting from the calculations for the three case studies.

shows that the relationship of cost factors for the different devices is the same; i.e., for any single case, the cost rank same regardless of which cost factor is used. It is found the ESP is the least expensive control method for the cases of med high sulfur coal. In the case of low sulfur coal, however, the is shown to be more expensive than a hot ESP or either of the filters. Comparing the hot ESP and baghouse, the former is me effective for low sulfur coal. In medium and high sulfur coal

cases are shown in Table 2. These input parameters were used

the hot ESP is more expensive than the cold ESP but less expen either of the baghouses. The cost of the baghouse remains fa

pendent of coal characteristics. Clearly, the high gerating equipment cost of scrubbers make them uneconveries life they are only for particulate control.

A comparison of energy consumption factors to rediffe trol devices is presented in Table 5. In terms of total energ tion, the results show that a cold ESP ranks as the most eners device, followed by a baghouse and then a hot ECF. Particular are shown to be the highest energy consumers. From the data of

it is evident that the high energy consumption of complibers as is, in part, due to stack gas reheat and heat loanen, remnent example, in the case of a scrubber with Pennsylvania wal, in energy are required for stack gas reheat in comparison to 18.1 energy for the operation of the scrubber.

Fundamental System Characteristics of Sample Gases Table 2.

System Characteristic Items

Items	Sample Gase 1	Sample Gase 2	Sample Gase 3
Plant site (mine-mouth plant)	Roscbud Gounty, Montana	Franklin Gounty, Illinois	Westmoreland County, Pennsylvania
Goal source	Rosebud County, Montana	Franklin Gounty, Illinois	Westmoreland Gounty, Pennsylvania
Goal cleaning	Level 1	Level 1	Level 1
Goal characteristics ^a			
Moisture	13.6	4.10	5.0
Ash	7.6	7.20	22.0
Sulfur	09*0	2,58	3.23
Garbon	00°09	72,30	00*09
Hydrogen	5.4	5.4	5.4
Nitrogen	1.6	1.6	1.6
Heating value, Btu/lb	10,116	12,768	10,912
Regulations	New Source Performance Standards (NSPS), 1.e., 0.03 1b/10 ⁶ Btu	New Source Performance Standards (NSPS), 1.e., 0.03 lb/10 ⁶ Btu	New Source Performance Standards (NSPS), 1.e., 0.03 lb/106 Btu
Boiler type	Pulverized coal-fired dry bottom boiler	Pulverized coal-fired dry bottom boiler	Pulverized coal-fired dry bottom boiler
Gapacity ^b	500 NWe total	500 MWe total	500 MWe total
^a Weight percent as received.	/ed•	ika dilan dia dan dia dan dan dan dan dan dan dan dan dan da	

 $^{^{}m b}$ The power consumed internally for the operation of the control equipment is not considered.

	Low	Sulfur Montana Ro	sebud Goal (Case L
Migration velocity,	0.110	0.25	-

Migration velocity,	0.110	0.25	-	44
ft/sec Collecting plate area,	1,330,281	840,966	•	-
ft ² Specific collector area,	811	513	-	-
ft ³ /1,000 acfm		_	956.595	583,282
Gross cloth area, ft ²	•	1.0	4.72	3.73
Pressure drop, in. WG	1.0	1.0	-	-
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft ³	•	-	,	
	Medium Su	lfur Illinois N	o. 6 Coal (Case 2)	
Migration velocity,	0.418	0.30	-	-
ft/sec		410 700		_
Collecting plate area,	307,336	613,733	-	
Specific collector area, ft ³ /1,000 acfm	203	282	-	-
Gross cloth area, ft ²	-	•	885,112	632,22
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft ³	-	•	-	-
	High S	Gulfur Pennsylva	nia Coal (Case 3)	
Migration velocity, ft/sec	0.386 ^d	0.30	-	-
Collecting plate area, ft ²	428,971	789,979	-	•

ft ² Specific collector area,	203	282	•	-
ft ³ /1.000 acfm	203	-		
Gross cloth area, ft ²	-	-	885,112	632,223
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft ³	•	-	•	-
	Hizh	Sulfur Pennsylva	nnia Coal (Case 3)	
Migration velocity,	0.386 ^d	0.30	-	-
ft/sec				
Collecting place area, ft ²	428,971	789,979	-	-
Specific collector area, fr ³ /1,000 acfm	275	354	-	-
Gross cloth area, ft ²	-	-	909,328	649,250
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1.000 fr ³	-	-	-	-

aRequired particulate collection efficiency per the proposed NSPS of 0.03 lb.106 Btu: 99 5% bRequired particulate collection efficiency per the proposed NSPS of 0.03 lb/10⁶ Btu: 39.4%

cRequired particulate collection efficiency per the proposed NSPS of 0.03 $1b/10^6$ Btu: 99.3% $^{
m d}$ Migration velocity is lower than for medium sulfur case due to the high ash content of coal

Table 4. Particulate Control Cost Analysis

Control Device	Total Installed Cost ^a (1978 dollars)	Total Installed Cost ^a and Inst. Elec. Capacity Charge (1978 dollars)	Aggregate Cost of Ownership and Operation Over 30 Years (1978 dollars)		unualized Operation ^b Mills/kWh ^C	Annual Oper: and Mair 1978 dollars
					~	······································
		Low Sulfur M	ontana Rosebud Coa	al (Case 1)		
Cold-side ESP	18,633,567	19,209,238	72,947,000	6,604,946	1.7735	220,642
Hot-side ESP	11,214,934	12,623,368	60,038,000	4,416,378	1.1872	423,124
Reverse flow baghouse	15,605,788	17,969,442	141,987,000	7,921,770	2.1295	1,397,052
Collapse + shake bag- house	14,645,403	16,718,784	126,029,000	7,033,680	1.8908	983,507
Scrubber	19,504,958	27,334,137	224,268,000	10,251,220	2.7557	2,848,311
		Medium Sulf	ur Illinois No. 6	Coal (Case 2)		
Cold-side ESP	5,289,612	5,382,821	27,041,000	2,061,167	0.5541	202,048
Hot-side ESP	8,725,309	9,810,970	53,519,000	3.607,477	0.9698	536,183
Reverse flow baghouse	15,085,623	17,131,695	134,721,600	7,620,659	2.0486	1,544,013
Collapse + shake bag- house	14,184,497	15,961,988	113,408,000	6,749,633	1.8144	1,101,698
Scrubber	19,653,669	25,246,368	245,204,000	10,703,545	2.8773.	3,715,188
		High Sul	lfur Pennsylvania	Coal (Case 3)		
Cold-side ESP	7,268,919	8,108,135	35,649,000	2,798,796	0.7524	261,617
Hot≈side ESP	11,252,677	12,695,721	65,872,000	4,587,859	1.2333	644,957
Reverse flow baghouse	15,808,259	19,473,208	139,772,000	3,065,957	2.1683	1,616,646
Collapse + shake baghouse	14,877,322	18,266,341	123,377,300	7,175,971	1.9290	1,163,349
Scrubber	21,167,265	34,944,548	333,900,000	14,284,449	3.8399	5,965,479

anstalled cost includes equipment and installation costs of the control device and associated ash handling ed liquor pumps, etc., and the land cost.

bTotal annualized cost equals the total of all the power costs associated with the operation of the control de operating labor, heat loss/cost of reheat, materials cost (lime and makeup water for scrubber), maintenance cand all the financial charges including depreciation, taxes, etc. For baghouses, maintenance excludes bag repment since it does not occur every year, but it is considered in the aggregate cost of ownership and operatio (Column 3).

^CSame as 5, expressed in mills/kWh, assuming 500-YWe total capacity and 7,440 operating hours per year.

dSame as b but excludes financial charges.

^{*}Same as d, expressed in mills/kWh, assuming 500-MWe total capacity and 7,440 operating hours per year.

Control Device	Electrical Power (MWe)	Heat Energy Usag (MWe)	e Energy Cost (1978 dollars) ^C
	Low Sulfur	Montana Rosebud C	oal (Case 1)
Cold-side ESP Hot-side ESP Reverse flow baghouse Collapse + shake baghous Scrubber	8.6721	0.0000 1.1568 ^a 0.0000 0.0000 13.2957 ^b	59,486 325,628 233,581 183,285 2,161,362
	Medium Su	lfur Illinois No.	6 Coal (Case 2)
Cold-side ESP Hot-side ESP Reverse flow baghouse	0.4604 1.0075 1.4844	0.0000 1.0704 ^a 0.0000	157,557 467,501 508,011

Total Annual

а P1

Equivalent of

Collapse + shake baghouse Scrubber	1.1619 6.1950	0.0000 12.3022 ^b	397,665 2,961,870
	Sulfur	Pennsylvania Coal (Case 3)
Cold≃side ESP	0.5980	0.0000	205,116
Hot-side ESP	1.2690	1.0997 ^a	561,267
Reverse flow baghouse	1.6692	0.0000	572,523
Collapse + shake baghouse	1.3380	0.0000	458,911
Scrubber	15.2598	12.6388 ^b	6,098,600

and for the heat energy portion an energy cost of \$1.75/10⁶ Btu is assumed.

^aIn converting the heat loss across hot ESP to an electrical power equivalent, a conve

efficiency of 38.8% (same as the default value for the plant overall thermal efficien

In converting the stack gas reheat requirement for a scrubber to an electrical power it is assumed that steam is used for reheat and the efficiency of a steam-electric tu SIn computing the total energy cost, the local power cost is used for the electrical p

hand calculator. A computer program has also been prepared as part of the work done for DOE on this project. The program is an aggregate of the individual models and thus provides for easy application of the models to any given situation.

As illustrated in the case study analysis, use of the model provides a means of comparing control device options based on any or of the following cost criteria:

- Installed cost,Total annualized cost, \$/year or mills/kwh,
- . Operating cost, \$/year or mills/kwh, and
- Aggregate cost of ownership and operation over lifetime.

Further, control device comparisons can be made based on en consumption expressed as:

- . Electrical power required, MWe,
- . Electrical power equivalent of heat,
- . Total power as a percentage of plant capacity, and
- . Annual cost of energy.

The above comparison of energy and economic impacts of various controoptions provides a valuable means for selecting the optimum method of control for any given system specifications, including power plant si coal characteristics, and emission limits.

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INTRODUCTION

An important characteristic of most Western coals is that they cont

significantly less sulfur than the 2 to 3 pct sulfur content typical of coals in the Interior and Eastern coal regions. The sulfur content of Western coals averages about 0.7 pct, and an average sulfur dioxide removen efficiency of only 30 to 40 pct is required to meet the Federal standard 1.2 lb SO2/MM Btu. At the present time, lime or limestone wet scrubbers the most commonly used methods for power plant sulfur dioxide emission control. Industrial acceptance of this technology has been slow due to large capital investment requirements, poor operation reliability, and problems associated with sludge disposal. The majority of the lime and limestone systems are located on utility boilers burning high-sulfur Interior and Eastern Province coals. In the West, however, where coal deposits

contain significantly less sulfur, several innovative flue gas desulfuri

One innovative FGD technique developed by the Grand Forks Energy Te

tion (FGD) techniques are being developed.

has had a significant impact on FGD technology.

nology Center (GFETC) is the utilization of alkali in Western coal fly a in a wet scrubber in lieu of lime or limestone. Studies at GFETC (1) has shown that sufficient amounts of alkali metals, such as calcium, can be leached from fly ash to provide a means of controlling sulfur dioxide emissions from utility boilers burning Western coals. At present there nearly 2600 MW of generating capacity controlling sulfur dioxide emission using fly ash alkali. Additionally, approximately 4200 MW of generating capacity are currently under construction or being designed which will utilize the fly ash alkali (FAA) system. These figures include only screens designed for sulfur dioxide control, and not those scrubber systems designed for particulate control on Western boilers, and in which some

A more recent trend in the West has been the use of spray dryers for sulfur dioxide control. This FGD process is based on injecting a concert trated slurry of alkali into the flue gas and atomizing the slurry to process transfer of the sulfur dioxide into the absorbent droplets. The figas is maintained above dew point temperatures, thus eliminating reheat requirements. The alkali reagent ends up as a fine particulate and is collected, along with the fly ash particulate, by a fabric filter or an

sulfur dioxide removal occurs. The utilization of Western fly ash alkal

electrostatic precipitator (ESP). The spray dryer FGD concept appears suitable for power plants burning Western coals, and at least one Wester utility with a new 450-MW plant will employ this concept for sulfur diox control.

water is required. Additionally, dry methods of FGD would be attractive utilities requiring a retrofit installation. This type of dry process been under investigation at GFETC since 1975. The materials investigat date are nahcolite and trona. The application of these materials involdirect injection into the flue gas duct, followed by collection of the sulfur capture agent, along with coal fly ash, using a baghouse or elec

static precipitator. Thus, there would be no complex chemical equipmen operate, nor flue gas reheat or water requirements, and capital equipme expenditures would be minimal.

The present paper presents a summary of past and present results obtained on a 5000-acfm (saturated) and a 130-scfm pilot plant wet scrulaboratory kinetic studies on dry adsorption of sulfur dioxide using na colite and trona, and pilot plant results on dry adsorption of sulfur d

2. ASH ALKALI FGD

tion.

An important characteristic of most Western coal ashes is their hi

by duct injection of nahcolite and trona followed by baghouse and ESP c

alkali content. In general, the alkali content tends to be highest in lignites, and progressively less prevalent in the subbituminous and bit nous coals. As with Western coal ash content, the ash alkali content c vary widely, ranging from under 10 pct to over 50 pct, with significant variations from mine to mine, and even between locations within a single

more recently, on a 5000-acfm pilot plant scrubber operating on a side-of flue gas from a 238-MW cyclone-fired boiler.

<u>Laboratory Studies</u>

mine. Studies on the utilization of Western coal fly ash alkali in a wascrubber were pioneered at GFETC using a 130-scfm pilot plant scrubber a

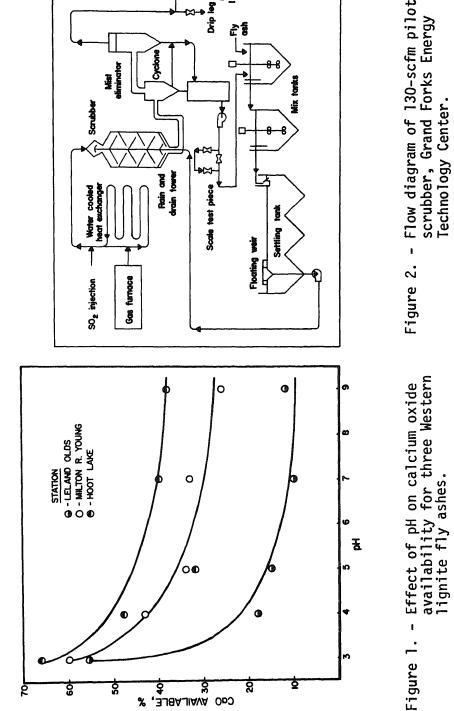
Laboratory studies at GFETC have shown that the fly ash alkali can solubilized into an aqueous media, and that solubilization is primarily

function of pH. Figure 1 illustrates the calcium oxide availability as function of pH for three North Dakota lignite fly ashes. The data were generated using batch leach procedures (1) and, in general, indicate an increase in the amount of calcium oxide as the solution pH decreases. Similar trends are evident for most Western coal fly ashes. There are,

Similar trends are evident for most Western coal fly ashes. There are, however, differences in fly ash leach characteristics from different min and power plants. The calcium oxide content of the three fly ashes show figure 1 are nearly identical; however, the percentage of available calculations.

figure 1 are nearly identical; however, the percentage of available calcat pH 7 varies from about 10 pct to about 40 pct. As the solution pH decreases, however, the differences in solubilities become less significant tend to approach similar values. The variations in alkali solubilities

can be attributed to differences in chemical composition of the original coal, and also to differences in the boilers from which the fly ash was derived. The alkali solubility data do indicate that significant amount calcium alkali can be leached from the fly ash for use in a contract.



Drip leg

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operating conditions (liquor pH values); however, there is often ample ash alkali available to react with sulfur dioxide in a wet scrubber.

Pilot Plant Studies

The 5000-acfm pilot scrubber was used to conduct a test program u a cooperative agreement among Combustion Equipment Associates (CEA), A D. Little Company (ADL), Minnkota Power Cooperative (MPC), Square Butt

Tests at GFETC have been conducted using a 130-scfm pilot plant s ber, shown in figure 2, and a 5000-acfm pilot plant scrubber at Center North Dakota, shown in figure 3. Objectives of tests using the 130-sc pilot scrubber have been to determine sulfur dioxide removal efficienc calcium sulfate saturation levels and scaling rates as a function of s gas sulfur dioxide concentrations, fly ash add rate and alkali content supplementary alkali requirements, levels of recirculated suspended so liquid-to-gas ratios, amount of makeup water, and total dissolved soli (2,3,4).

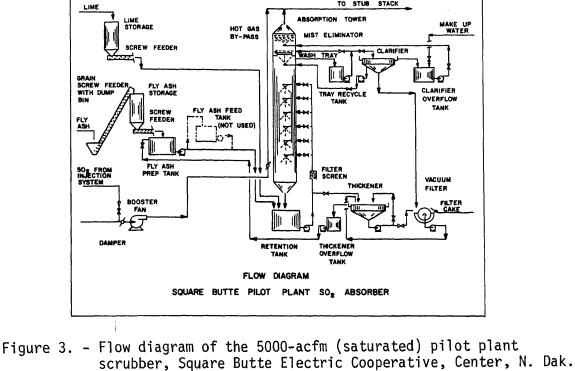
Electric Cooperative (SBEC), Minnesota Power and Light Company (MP&L), GFETC. The four major objectives of the cooperative program were: 1) generate design criteria and determine operating conditions for a 450-scrubber using only fly ash alkali; 2) To conduct a parametric study a operating conditions representative of steady state using fly ash in a typically available from both cyclone- and pc-fired boilers; 3) To inv gate low pH scrubbing to increase utilization of the fly ash alkali; a To investigate the effects of high sodium and magnesium concentrations ash alkali utilization and sulfur dioxide removal efficiencies at low to-gas ratios (5,6,7,8).

parameters investigated on the 5000-acfm pilot scrubber. The objective the tests were to characterize sulfur dioxide removal efficiency, calcounties of scale formation, calcium sulfate saturation slurry retention time, and level of recirculated suspended solids on the scfm pilot scrubber. This paper will compare selected results obtained the 130-scfm pilot plant to results obtained on the 5000-acfm pilot plant.

The current test program on the 130-scfm pilot scrubber duplicate

Figure 4 illustrates the sulfur dioxide removal efficiency and ca oxide utilization as a function of stoichiometric ratio. The inlet su dioxide and liquid-to-gas (L/G) ratio were maintained at nominal value 1000 ppm (dry) and 60, respectively. The level of suspended solids va from about 0.5 pct to about 12 pct. The averaged data obtained on the acfm pilot scrubber (6) are represented by the solid curve for sulfur

dioxide removal, and the dashed line for calcium oxide utilization. To squares represent sulfur dioxide removal efficiency, and the circles resent the corresponding calcium oxide utilization obtained on the 130-s



UTILIZATION, REMOVAL, 70 70 _{හි} ලෙ 60 S 50 50 40 40 0 2.0 0.5 STOICHIOMETRIC RATIO, CaO/SO2

Figure 4. - Sulfur dioxide removal and fly ash CaO utilization as a function of stoichiometric ratio at 1000 ppm SO₂ and a L/G of 60 gal/1000 acf. Data obtained from the 5000-acfm pilot plant scrubber are denoted by the dashed and solid

pilot plant conditions will be obtained, and will provide a means of jecting pilot plant results to a full-scale scrubber using any reager

The degree of calcium sulfate saturation is related to scaling in a Western scrubber. Control of scaling must be approached different

for low-sulfur Western coals than for Eastern coals, primarily due to high state of sulfur oxidation. Control of scale formation in the falkali system will depend most directly on maintaining a relatively oph, and on circulating a sufficiently high level of suspended solids allowing sufficient time and mixing to desaturate calcium sulfate in solution. The recirculated suspended solids are composed of calcium and undissolved fly ash particles, which can assist in maintaining that constant value. If the sulfur dioxide levels should significantly increase, the undissolved fly ash suspended solids react with the exception.

The effects of suspended solids and retention time on calcium solutions.

The effects of suspended solids and retention time on calcium solution on the 130-scfm pilot plant scrubber are not clearly defined at a using suspended solids ranging from 0.5 pct up to 11.5 pct indicated on saturation, remaining approximately constant at about 200 perfect on saturation, remaining approximately constant at about 200 perfect on the saturation of 1 to 6 pct, and no effect from 6 pct up to about 12 pct. The saturation is a saturation of 1 to 6 pct, and no effect from 6 pct up to about 12 pct. The saturation is a saturation of 1 to 6 pct, and no effect from 6 pct up to about 12 pct.

values were calculated using activity coefficients. Data generated liquor retention times from 4 minutes to 16 minutes also indicate no

on calcium sulfate saturation, and the values were generally constant about 200 pct. However, scale formation was not detected during expension either the 130-scfm pilot plant scrubber or on the 5000-acfm pilot scrubber.

One characteristic of scrubbing with fly ash alkali is the high dissolved solids, specifically magnesium, sodium, and sulfate. The

levels, which represent 99 pct of the soluble sulfur forms in the soliquors from the 130-scfm and 5000-acfm pilot plant scrubbers, may react to 8 pct and contribute directly to the high saturation values. The sium and sodium levels are also high, reaching concentration levels pct. The overall effect of the high sulfate levels is to increase to cium sulfate saturation values, with the magnesium and sodium levels

decreasing the saturation values.

A summary of physical characteristics of sludge (8) generated d two-week material balance test on the 5000-acfm pilot plant scrubber shown in Table 1.

Porosity..... Moisture.....pct.. Unconfined compressive strength.....kg/cm²...

Range of values for ten samples.

0.64 to 0.77

23 to 38

1.0 to 2.5

Since the predominant sulfur form in the scrubber liquor is sulfate and is readily dewatered. Pozzolanic activity due to unreacted fly ash be visually observed, and is also demonstrated by the relatively large va

sludge material is enriched in calcium sulfate in addition to unreacted Therefore, the resulting sludge has excellent settling characterist

when disposed in a landfill.

DRY ADSORPTION OF SULFUR DIOXIDE

of unconfined compressive strength shown in Table 1. The permeability coefficient for the sludge material ranged from 2×10^{-6} cm/sec to 6.5×10^{-6} cm/sec. These values are one to two orders of magnitude less than lime/ stone sludge materials and should pose less of a threat to the environment

Many utilities in the West are located in areas where water supplies A true "dry" sulfur dioxide removal system would be an attractive alternative to a wet scrubber system. Additional advantages of a dry FGI system are: 1) no complex chemical plant to operate; 2) high reliability 3) immediate response to fluctuation in sulfur dioxide levels; 4) disposi a dry waste material; 5) less capital investment requirements; 6) lower ating expenses; and 7) more readily adaptable to retrofit situations. The FGD technology may be more suitable for utilities burning Western coals the low sulfur content would require smaller quantities of sorbent mater

to meet the existing NSPS of 1.2 lb SO₂/MM Btu, or the proposed standard 85 pct removal. The objectives of the GFETC dry adsorption program are to determine

suitability of various materials as dry adsorbents, and to conduct large scale parametric tests on promising adsorbents. Two promising materials nahcolite and trona, which are naturally-occurring mixtures of sodium ca bonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃). This report presents selected results on kinetic studies using laboratory batch-type fixed-be-

reactors, and on pilot plant tests using a 75-lb/hr pulverized coal-fire

furnace with either a baghouse or an ESP for particulate control.

figure 5. Simulated flue gas of the desired composition was passed the reactor containing a thin bed of adsorbent. When nahcolite and trona are exposed to elevated temperatures, so bicarbonate is converted to sodium carbonate, resulting in a significan

change in the specific surface area. The bicarbonate-to-carbonate consion product is commonly said to be activated. Figures 6 and 7 illust effects of temperature and time on surface area for nahcolite and tronrespectively. For both adsorbents, the maximum specific surface area achieved at about 600° F. At temperatures above 600° F, the specific area decreased significantly due to sintering of the particle surface. sintering effect was verified by SEM photographs (10). The data indic that the bicarbonate-to-carbonate conversion occurs more rapidly for n (see fig. 6) than for trona (see fig. 7), especially at temperatures a 500° F. Additionally, nahcolite has a higher specific surface area th over all temperature ranges. In the present experiments, both adsorbe preheated at 600° F for two hours to ensure an equivalent starting mat for all test conditions. Future plans include redesigning the reactor

to allow charging the adsorbents directly into the preheated batch rea

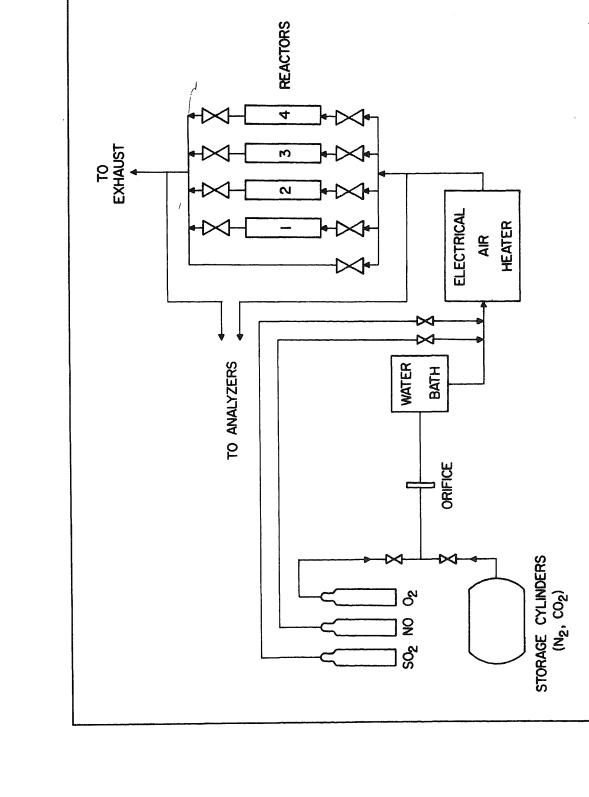
with gas flow established. Figure 8 illustrates the effect of temperature on sulfur dioxide tion using nahcolite. In general, the sulfur dioxide adsorption profi indicate an initial rapid increase which levels off to a relatively co value for the time range investigated. For the time range of zero to seconds, the adsorption rate increases with temperature up to about 65 However, the data collected at 750° F indicate a slight reduction in a

temperature, and residence times.

sodium sulfate. For both the 0.5 mm and 0.19 mm reacted particles, th investigation indicates a sodium sulfate ash layer penetration of abou

tion. The decreased adsorption at 750° F may be attributed to sinteri the particle surface, causing a decrease in specific surface area. Figure 9 illustrates the effect of particle size on sulfur dioxid adsorbence using nahcolite. The results indicate that as the particle decreases from an average particle diameter $(\overline{D}p)$ of 0.5 mm to 0.09 mm, amount of sulfur dioxide adsorbed was doubled. The adsorbent utilizat the 0.09 mm particles was about 98 pct after 200 seconds. An examinat the reacted nahcolite using SEM techniques indicated that the lower ad tion of the larger particles was due to pore blockage by an ash layer

mm. These results indicate that an optimum particle size exists, belo which additional adsorbent size reduction is not beneficial. The opti adsorbent size would depend on the specific application, gas-solid con



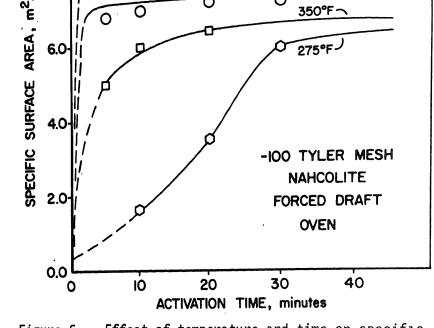


Figure 6. - Effect of temperature and time on specific surface area for nahcolite.

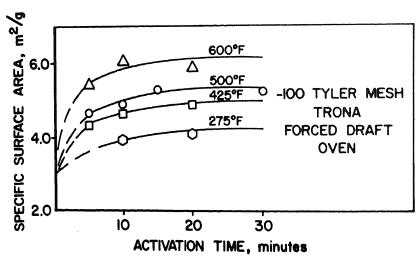


Figure 7. - Effect of temperature and time on specific surface area for trona.

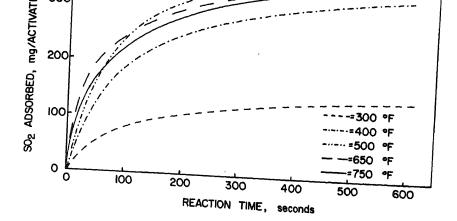


Figure 8. - Temperature effect on nahcolite sulfur dioxide adsorbance.

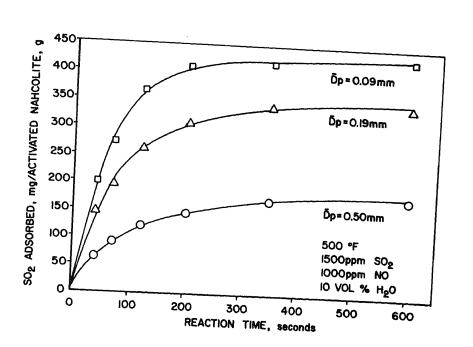


Figure 9. - Effect of nahcolite particle size on sulfur dioxide adsorbance.

and trona at identical experimental conditions. The data indicate adsorbence for trona compared to nahcolite at each condition invest Their results may be attributed to the lower specific surface area (see fig. 7). However, the differences may be less significant in applications where lower temperatures or longer retention times are tered, or smaller trona particles are utilized. Analyses of reacted nahcolite and trona obtained from the above for nitrites and nitrates indicate little nitric oxide adsorption. when tests with nahcolite were repeated without sulfur dioxide in t gas, appreciable amounts of nitric oxide were adsorbed, as shown in

The dashed line represents nitric oxide adsorption in the absence of dioxide. The solid line represents nitric oxide adsorption in the of 1500 ppm sulfur dioxide. The data indicate significant nitric of adsorption in the absence of sulfur dioxide, and the adsorbent util

Figure 12 illustrates the sultur aloxide adsorbence using both

approaches 97 pct for a reaction time of 5400 seconds (90 minutes). results indicate a competitive reaction between sulfur dioxide and oxide for the active sites of the nahcolite adsorbent, with the sul dioxide dominating the reaction kinetics. Preliminary data indicat greater amounts of nitric oxides are adsorbed at 300° F than at hic peratures. This apparent decrease in adsorption may be due to ther instability of the reaction product; however, additional studies ar Both nitric oxide and nitrogen dioxide adsorption will be investigagreater detail in future work.

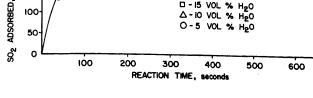
Pilot Plant Studies Tests have been performed utilizing the GFETC 75-1b/hr, pc-fir

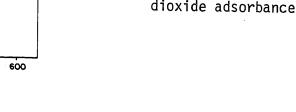
pilot ESP facility, shown schematically in figure 14. The subbitum burned in this study was provided by Utah Power and Light (UP&L) fr Kemmerer Mine at Kemmerer, Wyoming. UP&L also provided the nahcol obtaining them from the Superior Oil Company.

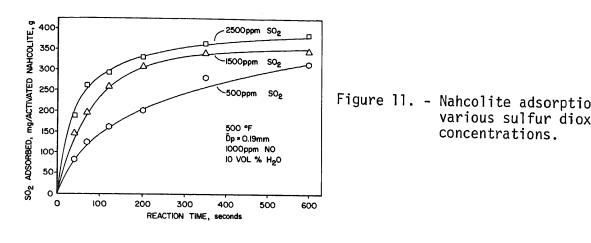
The pilot plant program was designed to study dry sulfur diox tion as a function of adsorbent material, injection temperature, re time, stoichiometric ratio, adsorbent particle size, and collection operating temperature under simulated power plant conditions. Flue sulfur dioxide removal could occur in any one of three regions in s

application: 1) during sorbent suspension in the flue gas, 2) dur tion in an electrostatic precipitator, and 3) during collection in

filter (baghouse). The sulfur dioxide concentrations were maintain range of 850 to 1000 ppm, approximating the combustion of Kemmerer a one pct as-received sulfur content. The present results represen mary of the work completed to date.







concentrations.

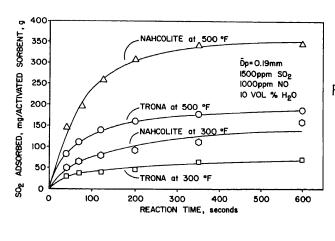


Figure 12. - Comparison of nahco and trona sulfur di adsorption at two temperatures.

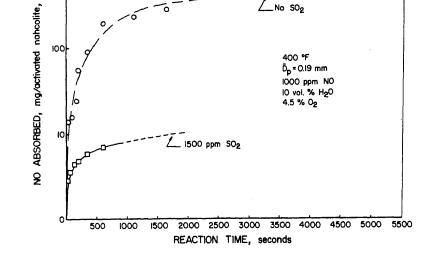


Figure 13. - Nitric oxide adsorbance using nahcolite with and without sulfur dioxide.

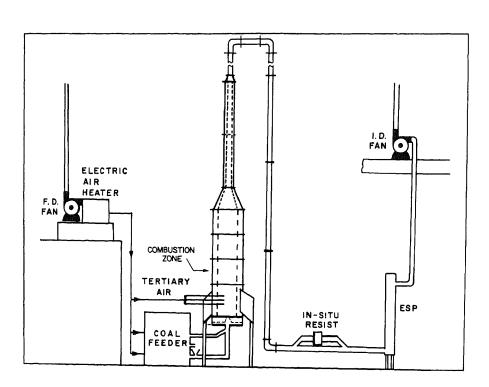


Figure 14. - Schematic of 75-lb/hr pc-fired pilot plant combustor at GFETC.

pct and overall utilizations were nearly constant at 22 pct. These results would indicate an optimum utilization of about 22 pct regardless of adsorben material or stoichiometric ratio. From 62 to 100 pct of the overall sulfur dioxide removal occurred in zone A (flue gas above 1400° F). The 39 pct maximum removal observed under case I conditions is approximately equivalent to that fraction of the total sulfur dioxide resulting from combustion of the coal (320 ppm out of 925 ppm). Results obtained under case 2 conditions indicate a range of sulfur dioxide removals from 32 to 99 pct at stoichiometric ratios of 0.8 to 2.6. Virtually all of the removal occurred in zone A. Utilizations averaged 41 pct with, again, very little variation with stoichiometric ratio or adsorben material. These results indicate that nearly all of the sulfur dioxide

into the furnace burner were performed in two ways. In the first case, the makeup sulfur dioxide (required to increase the normal sulfur dioxide level of approximately 320 ppm to the desired level of 925 ppm) was injected after the combustion gases had been cooled to below 2000° F. In the second case, the makeup sulfur dioxide was injected along with the coal into the burner. Data from these tests are summarized in Table 2. In the first case at stoichiometric ratios of 0.9 to 1.8, sulfur dioxide removals ranged from 21 to 39

removal occurs at temperatures above 2000° F when the adsorbents are injected into the flame region. The events occurring in such a process most likely correspond to those postulated for the action of sodium in promoting ash fouling of heat exchange tubes in coal-fired boilers (11). The sodium

material volatilizes in the coal flame, forming a reactive vapor which combines rapidly with gaseous sulfur dioxide or sulfur trioxide to form a fine sodium sulfate particulate when cooled. Burner injection of sodium materials for sulfur dioxide control could not be recommended due to the near certaint that severe ash fouling would result in the boiler superheat and reheat To evaluate the potential ash fouling problem, an experiment using

nahcolite injected into the burner was conducted using the 75-1b/hr, pc-

fired ash fouling furnace at GFETC. The result was formation of a molten, glassy, flowing slag on the simulated secondary superheat tubes. This most assuredly would be an impossible condition in a full-scale boiler.

Adsorption in Flue Gas Suspension

Tests to evaluate the sulfur dioxide adsorbence of nahcolite and trona in a flue gas stream, with injection temperatures ranging from 360 to 1515° F, indicate an optimum injection temperature of about 650° F for both The existence of an optimum injection temperature is in agreemen

with the results obtained in the laboratory kinetic study (see figures 6, 7,

and 8). The data obtained at 650° F are presented in Table 3.

ed into the flame	Zone C	Zone A + B + ESP	Residence Removal, zati
ur dioxide adsorption results with adsorbent injected into the flame	Zone B	Prior to ESP	Residence Removal, zation, Residence Removal, zation, Residence Removal, zati
TABLE 2 Sulfur dioxide adsorption r	Zone A		Nometric Residence Removal, zation, Ratio time, sec. pct pct
Г			terial

d into t	Zo
oxide adsorption results with adsorbent injected into t	Zone A Zone A + Flue Gas Zone A + Flue Ga
oxide adsorption r	Zone A Prior to 1400° F Utili- Removal, zation,

sorbent injected into the flame	Zone C
sorbent injected	Flue Gas

107		Residence	3	time, se		
U COL	Utili-	Removal, zation,	100	100		

time, sec.

pct

Zone C	A + B +	Remova	3	21.6	39.1
	Zone A + B	Residence		5.0	4.0
Gas	(1+111-	zation, pct		21.7	4.17

zati 의 23.

22.

26.5

4.7

20.7

24.6

3.7

18.6

22.1

2.9

1.18

na

19.9 16.5 39.1

3.9

19.3 13.2 21.4

17.7 13.2 39.1

3.1

0.92 1.00 1.83

ncolite colite

oolite

SE $1:^{1/2}$

42.

31.6

6.0

42.6

31.689.4

5.0

42.6

31.6

3.1

0.79

colite colite

2:2/

39.

53.4 98.8

6.1

39.9 37.8

53.4 98.3

5.0

39.9

53.4 97.5

3.1

1.34 2.60

Ø ₫

dsorbent into burner along with coal, makeup sulfur dioxide injected downstream (flue gas below 2000° F).

dsorbent and makeup sulfur dioxide injected into burner along with coal.

Nahcolite	200	650	3.5	1.47	45.6	31.0
	200	650	3.2	1.84	61.2	33.3
Trona	100	6 4 0	3.1	1.96	33.0	16.7
	100	630	1.2	1.03	25.6	24.8
The data	a indicate	that, altho	ugh a sulfu	r dioxide r	emoval gre	ater than

60 pct was achieved in the best case, the low adsorbent utilization values

3.1

3.1

0.71

1.52

24.0

48.2

33.9

31.8

640

640

would probably make such a scheme unattrative for economic reasons. As the selected data illustrate, there is not a clearcut difference for in-duct sulfur dioxide removal between the minus 100 and minus 200 mesh nahcolite. As in flame injection, utilization of nahcolite adsorbent was independent o stoichiometric ratio at the conditions studied. There is some indication from the whole body of data obtained that below the residence times availab in a power plant, greater than three seconds, and at injection temperatures below the optimum 650° F, the finer material performs somewhat better. At injection temperatures above about 800° F, there is no apparent difference between minus 100 mesh nahcolite and minus 100 mesh trona. At injection temperatures near the optimum and below, the minus 100 mesh nahcolite has a distinct advantage. Although tests have not been run to evaluate a finer trona for duct sulfur dioxide adsorption, the data comparing the two size ranges of nahcolite would lead one to expect somewhat improved performance for a minus 200 mesh trona.

Adsorption in a Pilot Plant ESP

Nancolite

100

100

A series of tests were conducted to study the nahcolite and trona adso bents in systems which include an ESP. The motivation was twofold: 1) to evaluate such a system for sulfur dioxide removal, and 2) to determine the effect of the injection of relatively large quantities of sodium material o During ESP operation, the overall sulfur dioxide removals a

adsorbent utilizations were increased an average of 55 pct above that occur ring in suspension. It is felt that this apparent improvement due to the presence of the ESP might not be as substantial in a full-scale precipitato At least two factors would tend to reduce the potential effectiveness of th increased flue gas residence time in a full-scale precipitator. In the fir place, the majority of the removal of the input particulate mass in a fullscale ESP occurs in the first few feet, significantly reducing the portion the apparent long residence time which is effectively adsorbent/flue gas Secondly, the collection electrode of the pilot ESP utilized resistivity, there was virtually no change in ESF mass removal efficiency. The doubling or tripling of the inlet particulate concentration, however, resulted in a twofold increase in the outlet particulate concentrations all cases studied.

Adsorption in a Pilot Plant Baghouse

temperature.

A series of tests were conducted to study the nahcolite and trona adsorbents in systems which include a baghouse. The pilot baghouse was substituted for the pilot ESP in the system illustrated in figure 14. To with nahcolite indicate that utilization in the baghouse was independent adsorbent size below 100 mesh, injection temperature, and stoichiometric ratio at baghouse cycles of 45 to 60 minutes. In these cases, adsorbent injection was maintained at a constant level for the entire cycle. The overall adsorbent utilizations fell in the range from 63 to 77 pct for a cases. More tests are required to evaluate the effect of baghouse operations.

The particle size of the adsorbent appears to be a significant factor when trona is used as the adsorbent, as shown in figure 15. The utilizate shown in figure 15 for the minus 200 mesh trona fall within the range definited for nahcolite (63 to 77 pct), indicating that properly sized trona be as effective as nahcolite when used in conjunction with a bahouse. Most tests are required to establish what additional parameters might significant factor.

Figure 16 illustrates an interesting aspect in the development of disulfur dioxide adsorption techniques utilizing a baghouse. In this case the trona at an overall stoichiometric ratio of 0.96 was injected during first 8 minutes of a 74-minute test. A series of such curves over a variof cycle durations and injection schemes should aid in the development of optimum dry adsorbent injection methods and baghouse designs for use in a sulfur dioxide removal system. Optimization of the system should incluevaluation of adsorbent injection techniques and baghouse cycling. In general, dry sulfur dioxide adsorption utilizing nahcolite and trona in quinction with a baghouse appears to have potential as a flue gas desulfur zation technique. Continuation of the current test program is certainly

warranted. Larger-scale testing to confirm the potential indicated by the work, as well as that of others (12,13) should be planned in the near fu

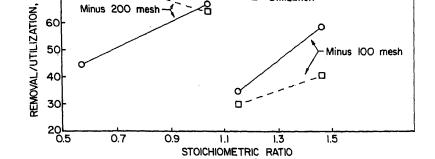


Figure 15. - Adsorbent utilization (denoted by dashed line) and sulfur dioxide removal (denoted by solid line) as a function of stoichiometric ratio using minus 100 and minus 200 mesh trona in a baghouse.

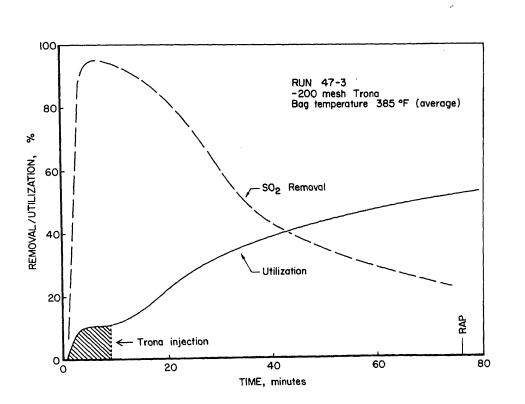


Figure 16. - Sulfur dioxide adsorption results utilizing minus 200 mesh trona with a baghouse and non-continuous adsorbent injection.

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September 1978

The literature on past and current global ${\rm CO}_2$ studies yields a perspective on the bounds of the potential atmospheric ${\rm CO}_2$ problem. During the last

Introduction

one hundred years or so, the release of fossil carbon as CO₂ has increased an exponential rate as shown in Figure 1. As a result, the concentration of CO₂ contained in the atmosphere has grown by about 12%, increasing from about 295 ppm by volume in 1960 (pre-industrial revolution) to the current level of 331 ppm. Except for short periods during World Wars I and II and the depression, the release rate of fossil carbon has increased at the rate of about 4.3% per year. At present, with no CO₂ emission controls, about 5 x 10⁹ metric tons of carbon per year as CO₂ are emitted to the atmospher by the burning of fossil fuels from worldwide sources. About 50% of this carbon can be accounted for by the increase in the CO₂ concentration of the atmosphere. The remaining carbon is assumed to be absorbed by the oceans and by the land biota, in unknown proportions. Deforestation considerations and the possibility of the release of CO₂ from the Pacific Ocean waters sout of the equator due to the "Southern Oscillation", a naturally occuring

phenomenon of unknown cause, tend to becloud the issue. A better understand

ing of the carbon cycle is definitely needed.

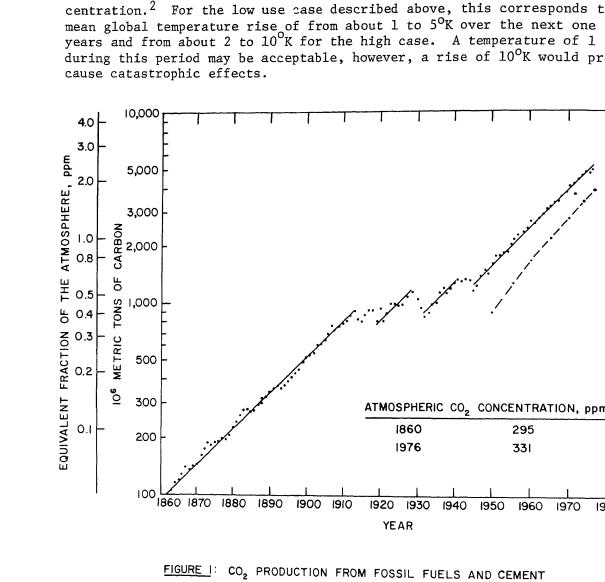
If the use of fossil fuels continued to grow at 4.3% per year until the estimated supplies thereof were exhausted, the use rate at the end of this period would be almost 64 times the current use rate, and the total CO_2 injected into the atmosphere, during this period, would be about 12 times the pre-industrial content of the atmosphere. Obviously, such a use pattern cannot be tolerated; however, based on more realistic assumptions, it is predicted that the concentration of atmospheric CO_2 , relative to the pre-industrial value, could increase by a factor of from about 2 (low use case) to about 5 (high use case) during the next one hundred years. The low use case corresponds to a fossil fuel growth rate of 2% per year until the

year 2025, followed by a symmetrical decrease as alternative and renewable energy sources become more available and the use of fossil fuels is dis-

4.3% with subsequent reductions in proportion to the ultimate fossil fuel supply that has been consumed. In both cases, about 50% of the emitted fossil carbon is assumed to be taken up by the oceans and land biota.

The high use case corresponds to an initial annual growth rate of

Of primary concern is the warming ("greenhouse") effect which could be produced by these increased ${\rm CO}_2$ concentrations due to the absorption by ${\rm CO}_2$ of a portion of the infrared radiation returning to space from the earth [the infrared absorption spectrum of ${\rm CO}_2$ shows strong absorption bands at



regime (the regular pattern of seasonal rainfall) as well as the earth albedo (reflection power). The amount of warming produced by a given concentration increase is estimated at 1 to 5°K per doubling of the CO

- WORLDWIDE LESS U.S. SOURCES

Increased concentrations of particulate matter (and aerosols) in t global air mass could produce a cooling effect by backscatter of incomisolar radiation and thus counteract, to some degree, the warming produc-

- WORLDWIDE

by increasing CO₂ levels. However, environmental emission regulations of particulates, as well as on other identified pollutants, have become more

a prudent strategy.

environmental effects of CO₂ discharge; accordingly, there are no regulation applicable to CO₂ emissions. Options for CO₂ control have received little attention and although preliminary evaluations indicate that control is theoretically possible, it may not be technically or economically practicable. It thus becomes important at this time to examine CO₂ control options to determine the technical feasibilities and the economic costs, should the nee arise for CO₂ control.

Impact of US Emissions

In order to determine the impact of fossil fuel use in the United State on overall (worldwide) CO₂ emissions, we have superimposed several points on Figure 1, based on US fuel use data for the years 1950, 1955, 1960, 1965, 1970, 1973. The points were obtained by subtracting the estimate

Since there is a chance that naturally occuring and/or anthropogenic opposing factors will not just counter the effects of increasing ${\rm CO}_2$ levels, it may be necessary to limit industrial ${\rm CO}_2$ emissions in the future. Up to the present, there has been practically no concern about the health or

Figure 1, based on US fuel use data for the years 1950, 1955, 1960, 1965, 1970, 1973, and 1976. The points were obtained by subtracting the estimat emissions of carbon (as CO₂) by US sources from the corresponding worldwide emissions for each of the above years, and thus indicate the quantities of carbon that would have been emitted if the US had not burned any fossil fuel during these years. The reduction in carbon (and thus in CO₂) by this hypothetical non-use of fossil fuels in the US ranges from 0.32 ppm in 1950 to 0.64 ppm in 1973 (and in 1976) as given in Table 1. However, during this period the percentage of the total yearly emissions contributed by the US decreased from 43% in 1950 to 27% in 1976. This is due to an increasing rat of fossil fuel usage in developing nations and a decreasing rate in the US. Furthermore, it is projected that the contributions to global CO₂ production by the US and Canada will decrease to about 8% by the year 2025. Developing nations will account for 36% of the CO₂ production, the USSR and Eastern Europe 27%, Asia 19%, Western Europe 7%, and Japan and Australia 3%.

Impact of Coal Utilization

probably would not be very effective.

Table 2 contains a source distribution of carbon (CO₂) produced from major worldwide sources during the years 1970 through 1976. For the year 1976, using the heating values of 18,000 BTU/lb of contained carbon for coal 22,400 BTU/lb carbon for fuel oil and 31,500 BTU/lb carbon for natural gas, and assuming that all fossil energy was produced by the burning of solid

fore, it would appear that a worldwide effort would be required to effective control the level of atmospheric CO₂. A unilateral effort by any one nation

coal, the carbon release to the atmosphere would have been roughly 6 x 10 metric tons or about 1.2 times the quantity actually emitted. Energy differences required in mining versus drilling, preparation, transportation, etc. and in combustion efficiencies were not taken into account. Note that

the weight ratio of CO_2 produced by the burning of coal to that produced by the burning of natural gas, for the same energy output, is about 1.8 and for

atmosphere would have been even greater than 6 x 10 metric tone, take inefficiencies in the gasification and liquefaction processes as will below. Thus, added reliance on coal for energy production could composite atmospheric release rate of CO₂, which has been increasing exponential since 1860.

Table 1

Incremental Atmospheric CO,

Concentration in ppm

Worldwide

0.74

0.92

1.18

1.47

2.00

2.27

2.38

Year

1950

1955

1960

1965

1970

1973

1976

2025 Est.

U.S. CONTRIBUTION TO ATMOSPHERIC CO₂ EMISSIONS COMPARED TO ALL OTHER WORLDWIDE SOURCES^{1,5}

U.S.

0.32

0.36

0.39

0.46

0.58

0.64

0.64

% U.S.

Contribution

43

39

33

31

29

28

27

8

% Others

57

61

67

69

71

72

73

92*****

			 -						
*Developing emissions.	nations	estimated	to	account	for	36%	of	total	worldwid

Impact of Alternative Energy Sources

The expected reduction in the US contribution to worldwide atmos

CO₂ emissions is partially attributed to the development and implement of alternative energy sources, which includes, nuclear (fission and figeothermal and solar. The impact of these alternatives in the US depends on the contribution to worldwide atmost contribu

geothermal and solar. The impact of these alternatives in the US dep to a great extent on four factors: (1) the demand growth for energy US, (2) the availability of the technology, (3) the capital and produ

costs, and (4) the supply of world petroleum sources and the demand of developing countries for petroleum and coal resources. Although unce

the energy demand no more than doubles is the second to the
the energy demand no more than doubles in the next 50 years, and the fossil
fractional use decreases about in half the US would then contribute approx-
imately the same amount as at present to the world atmospheric CO2 emissions,
as indicated by the CO ₂ Index in Table 4. However, the other countries would
exceed their present contributions as they develop technologically at a highe
rate. Eventually even these countries will acquire alternative energy source
and the CO_2 emissions may then become stabilized.

the US In the next 30 to 100 years as listed in Tables 3 and 4.

Source

Crude Petroleum &

N.G. Liquids

Coal

Lignite

Table 2

WORLD-WIDE $C0_2$ EMISSIONS BY SOURCE

All entries in 10^6 metric tons carbon as $C0_2$

1976
Distribution %

33.2

5.1

44.1

Natural Gas	545	583	614	646	659	665	675	13.4
Natural Gas Flared	90	94	100	110	113	105	113	2.2
Cement	82	88	93	95	95	100	99	2.0
Total carbon as ^{CO} 2	4254	4390	4560	4827	4876	4852	5047	
Incremental atm CO ₂ Conc. (ppm)	2.00	2.07	2.15	2.27	2.29	2.28	2.38	
U.S. Emissions Contribution	0.58			0.64			0.64	

In the interim, there is thus sufficient incentives, even when considering alternative energy sources, to systematically examine the technological and engineering factors for controlling CO_2 emissions. The systematic study would be of value for identifying candidate CO_2 control scenarios and to determine their technical and economic practicabilities. The environmental control technology of CO_2 may be of short term value for the US but of much more value in the longer term for worldwide purposes.

ANTICIPATED DISTRIBUTION OF ALTERNATE ENERGY SOURCES

FOR THE U.S. IN THE NEXT 50 TO 100 YEARS

			Perce	nt of Demai	na
Source	5	19	75	2025	2075
Fossil (coal, oil			90%	50%	30%
Nuclear (Fusion)	5	20	30
Solar			0	20	30
Hydro, Geotherma	1 and other	s	5	10	10
Total			100	100	100
		Table Table Table Table Table	NERGY GRO		
		1975			2025
Region	Quads	Fraction Fossil	CO ₂ *	Quads	Fraction Fossil
U.S.	75	0.90	67.5	150	0.50

1.00

0.97

175.0 1100

1250

242.5

0.84

0.80

* CO $_{2}$ index is product of Quads consumed and fossil fuel fraction.

175

250

Other Nations

World (total)

Logic for Constructing Scenarios for CO₂ Control Technology

The suggested logic for guiding the construction of CO₂ control s

The suggested logic for guiding the construction of CO₂ control is shown in block diagram form in Figure 2. The sequential steps to followed are:

Control Point Selection - Three potential control points (CO

LOGIC DIAGRAM FOR THE CONSTRUCTION OF SCENARIOS FOR CONTROLLING ATMOSPHERIC CARBON DIOXIDE STEP 2 STEP 1 STEP 4 STEP 6 CONTROL POINT CO, REMOVAL CO, RECOVERY REUSE PRÓCESS (CO, SOURCE) PRÓCESS PRODUCTS ALTERNATIVES SELÉCTION SELECTION SELECTION ATMOSPHERE 2. OCEANS INDUSTRIAL CO EMISSION SITES STEP 3 STEP 5 DISPOSAL DISPOSAL OPTIONS OPTIONS

latter site has the advantage of providing a source of relatively high CO2 concentration, while the former two provide more flexibility for site selection and simpler disposal or recovery and reuse logistics. A choice of control point limits the available choices of ${\rm CO}_2$ removal processes and will reflect on the size of operation, the number of required sites, removal efficiency, energy requirements, the comparative economics and on the overall

Figure 2

feasiblilty of operation.

Use of alternative fuels and energy sources are also considered as a potenti means of controlling atmospheric CO_2 .

 co_2 as a function of control point is contained in Tables 5A through 5E.

A listing of options for the removal, recovery, disposal, and reuse_of

- Removal Process Selection Once a control point has been selected, the next task is to survey available removal processes to determine those which appear to be feasible, and compatible, with the selected control point
- Identification of Disposal Alternatives for Captured CO_2 This tas involves the identification of alternatives which are available for disposin of the captured ${\rm CO_2}$ (Step 2) directly, that is without going through a ${\rm CO_2}$ recovery step, (e.g. desorption/sorbent regeneration). For example, if a naturally occurring, inexpensive and non-polluting CO2 adsorbent was availab
 - the spent sorbent containing the captured CO2 could be buried or stored in abandoned mine shafts rather than reused. A comparison between direct disposal versus ${\rm CO}_2$ desorption/sorbent regeneration would be made at the time of scenario evaluation since each alternative would represent a separate
 - no desorption step is required. CO₂ Recovery Process Selection - For a once through system, the quantity of sorbent consumed in absorbing or adsorbing CO2 would generally be very large because of the vast quantities of CO2 that would have to be

For the case of CO, extraction by refrigeration or distillation,

the level of atmospheric

- 5. Identification of Disposal Alternatives for Recovered $\rm CO_2$ This task is similar to that described under Step 3, above, except that $\rm CO_2$ would be in the form of a relatively pure gas, liquid or solid; that is, appreciable quantities of sorbents would not be present in the effluent (disposal) stream. Note that in the case of $\rm CO_2$ extraction by refrigeration, liquid or solid $\rm CO_2$ would be produced directly in the extraction step (Step 2) and therefore Steps 4 and 5 would not be required.
- 6. Identification of CO₂ Reuse Alternatives The last step in the process of scenario construction involves exploring and identifying reuse possibilities for recovered CO₂ (Step 4). Several possibilities have been identified in Tables 5A through 5E. One option which has been given some consideration is to catalytically convert the recovered CO₂ to methanol by reaction with hydrogen using a non-carbonaceous energy source. In some cases, it may be possible to proceed directly from CO₂ removal (Step 2) to CO₂ reuse as indicated by the broken line in Figure 2.

Since there are several key considerations in evaluating prospective control scenarios, e.g., energy and equipment requirements and sorbent property and losses, each scenario must be analyzed in some detail before realistic decisions can be made concerning its overall feasibility and comparative merits. A simplified approach could place emphasis on the wrong strategy and lead to false predictions and/or conclusions. However, the prime consideration in evaluating a $\rm CO_2$ control system which derives its energy from a fossil fuel source is the energy required by the control system. In these cases, additional $\rm CO_2$ would be generated in supplying energy to the control system and a point could be reached where more $\rm CO_2$ is generated in supplying energy to the control system than is removed from the control point.

Carbon Dioxide Generation as a Function of Fuel and Energy Source

There is a gradation in the amount of carbon dioxide produced per unit energy released depending on the type of fuel or energy source used. Table 6 lists a number of sources of fuels, the heating values and the unit ${\rm CO}_2$ generation in terms of mass of ${\rm CO}_2$ generated per unit energy released (1b ${\rm CO}_2/1000$ BTU) in utilization of fuel.

It is noted that the least CO_2 generation per unit energy output is produced by natural gas and by hydrogen from reforming of natural gas. The next smallest amount of CO_2 released is from natural petroleum products i.e. oil and gasoline. Further increase in unit CO_2 is given by wood, alcohol, and benzene. This is followed by coal and coke.

ATMOSPHERE

Absorption by Liquids

- 1. Water
- 2. Sodium carbonate
- 3. Potassium carbonate
- 4. Caustic
- Amines (e.g. monoethanolamine and diethanolamine)
- Other physical solvents (e.g. methanol and N-methylpyrrolidine)
- Other chemical solvents (e.g. ammonia and Alkazid)
- 8. Combined physical and chemical absorbents (e.g. Sulfinol)
- Physical a/o chemical solvents followed by caustic scrubbing

Adsorption by Solids

- 1. Naturally occurring sorbents (e.g. natural clays and zeolites)
- 2. Waste oil shale from retort operations
- 3. Molecular sieves

Extraction by Refrigeration

<u>Increased Planting of Land Biota</u> - photosynthesis

Absorption by Deep Ocean Waters - process used in conjunction with ocean thermal gradient power cycle.

Dilute Phase Methanation of Atmospheric CO₂-hydrogen supplied by non-fossil energy source.

II. OCEANS

Strip CO, with H2

Distillation or Steam Stripping

Acidification Followed by Degasification

III. MAJOR INDUSTRIAL
CO, EMISSION
SOURCES (e.g.
fossil plant stacks)

<u>Absorption by Liquids</u> - same alternatives as for the atmosphere.

Adsorption by Solids - same alternatives as for the atmosphere.

Extraction by Refrigeration

Advanced Power Cycle - air separation followed by combustion of fossil fuels by oxygen. Recovery of CO₂ from combustion by above processes

Use of Alternative Energy Sources

OLITONS FOR THE RELIGIONS, RESOURCES, ---OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT

OPTIONS FOR DISPOSAL OF CAPTURED CO2

I. **ATMOSPHERE**

CO2 Captured by Liquids

- 1. Evaporate water, then bury residue -carbonates and caustic sorbents only
- 2. Deep oceans water only

CO, Captured by Solids

1. Subterranean (e.g. abandoned mine shafts).

$\frac{\text{C0}}{\text{1.2}}$ Captured by Refrigeration Extraterrestrial

- 2. Deep oceans
- 3. Antarctic region
- 4. Subterranean

CO, Captured by Plants

1.2 CO, remains integral part of plant

CO₂ Captured by Deep Ocean Waters
1. Deep ocean

II. OCEANS

Co Captured by DistillationExtraterrestrial

- Deep oceans
- 3. Antarctic region
- 4. Subterranean

CC₂ Captured by Acid./Degas. 1. Extraterrestrial

- 2. Deep oceans
- 3. Antarctic region
- 4. Subterranean

III. MAJOR INDUSTRIAL CO, EMISSION SOURCES (e.g. fossil plant stacks)

CO2 Captured by Liquids - same alternatives as for atmosphere

CO, Captured by Solids - same alternatives as for atmosphere

CO, Captured by Refrigeration - same alternatives as for atmosphere

CO₂ Removed by Adv. Power Cycle 1. Extraterrestrial

- 2. Deep oceans
- 3. Antarctic region
- 4. Subterranean

Table 5C

OPTIGNS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

	CONTROL POINT	OPTIONS FOR RECOVERING CAPTURED CO2
I.	ATMOSPHERE	CO ₂ Captured by Liquids 1. Desorption by flashing 2. Desorption by distillation 3. Strip with gases, i.e., H ₂ , N ₂ , steam, etc. 4. Desorption by combined flashing and distillation or stripping 5. Electrolytic decomposition of scdium carbonate to form sodium hydroxide, H ₂ , O ₂ , and CO ₂ by non-fossil fuel source
		CO ₂ Captured by Solids 1. Decomposition by heating a/o stripping (e.g. by high pressure steam)
		CO ₂ Captured by Methanation 1. Absorb methane in a solvent, then desorb by flashing a/o distillation or stripping
II.	OCEANS	
III.	MAJOR INDUSTRIAL CO_ EMISSION SOURCES (e.g. fossil plant stacks)	CO ₂ Captured by Liquids - same alternatives as for the atmosphere. CO ₂ Captured by Solids - same alternatives as for the atmosphere. CO ₂ Captured by Refrigeration

Table 5D

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT

OPTIONS FOR DISPOSAL OF RECOVERED CO2

I. ATMOSPHERE

Gaseous CO₂
1. Extraterrestrial

Liquid CO,

- 1. Extraterrestrial
- 2. Deep oceans
- 3. Subterranean

Solid CO2

- 1. Extraterrestrial
- 2. Deep oceans
- 3. Antarctic region
- 4. Subterranean

II. OCEANS

III. MAJOR INDUSTRIAL CO, EMISSION SOURCES (e.g. fossil plant stacks)



Table 5E

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT

REUSE ALTERNATIVES FOR CAPTURED/RECOVERED CO2

I. ATMOSPHERE

Gaseous CO,

- 1. Catalytically convert CO₂ to gaseous a/o liquid carbonaceous fuels (methane, methanol, gasoline) by reaction with hydrogen, using non-fossil energy source (e.g. fission, fusion, solar)
- Decomposition of CO₂ to CO using nonfossil energy source (e.g. solar and nuclear radiation and high temperature heat), shift CO with water to form CO₂ and H₂; subsequently convert to carbonaceous fuels
- 3. React CO_2 with NH_3 to form urea fertilizer
- 4. Use CO₂ for controlled photosynthesis in greenhouses--plant products in biosphere a/o burn for energy production

Liquid CO,

- 1. Use for liquid CO₂ applications including industrial chemical uses
- 2. Use for displacing crude oil from reservoir rock.
- 3. Same alternatives as for gaseous ${\rm CO}_2$ after vaporization

Solid CO.

- Use for dry ice applications
- Same alternatives as for gaseous CO₂ after sublimitation

II. OCEANS

III. MAJOR INDUSTRIAL
CO, EMISSION
SOURCES (e.g.
fossil plant
stacks)

Fuel Type	Chemical Formula	Heating Value BTU/1b	CO ₂ generated 1b ² CO ₂ /1b fuel	CO ₂ generated 1b ² CO ₂ /1000 BTU	Energy generated kwh(e)/lb CO2 generated
Coke (ashless C)	С	14,100	3.67	0.26	
Bituminous Coal	CH _{0.8} 00.1	13,000	2.75	0.21	0.56
Gasoline & Fuel Oil (petrol. dist.)	(CH ₂) _n	20,800	3.14	0.15	0.90
Benzene	с ₆ н ₆	18,000	3.38	0.19	
Acetylene	с ₂ н ₂	21,500	3.38	0.16	
Methanol (wood alc)	сн ₃ он	10,000	1.38	0.14	
Methanol (syn. from coal)	сн ₃ 0н	10,000	2.75	0.28	0.42
Biomass (wood, cellulose)	(CH ₂ 0) _n	8,000	1.47	0.18	
Carbon Monoxide	CO	4,370	1.57	0.36	0.33
Natural Gas	сн ₄ .	24,100	2.75	0.11	1,07
SNG from coal gasification	СН	24,100	8.75	0.34	1.01
SNG Coal & Nuclear Hydrogen	CH ⁷	24,100	2.75	0.11	1.07
Hydrogen generated by:	н ₂	61,000	0	0	
Coal Gasification	H ₂	61,000	16.5	0.27	
Natural Gas Reforming	н ₂	61,000	7.0	0.11	
Nuclear-Electrolytic	H ₂	61,000	0	0	
Solar-Electrolytic	H ₂	61,000	0	0	
Geothermal-Electrolytic		61,000	2.44	0.04	

Finally it is noted that synthetic natural gas (SNG made from coal) and carbon monoxide (CO) generates the largest amount of ${\rm CO_2}$ per unit of energy released. Hydrogen produced by coal gasification generates less ${\rm CO_2}$ than SNG from coal. In determining the ${\rm CO_2}$ generated by synthetic fuels such as SNG, methanol and hydrogen from coal, the ${\rm CO_2}$ generated in the production process is included. Thus, ${\rm CO_2}$ generated from SNG (0.34) is 3 times greater than ${\rm CO_2}$ generated from natural gas (0.11). Geothermal energy releases certain amounts of ${\rm CO_2}$ per unit 1000 BTU which is estimated from a number of operating geothermal wells. Of course there is no ${\rm CO_2}$ generation if nuclear or solar energy is used to produce hydrogen fuel.

Control Source CO₂ Concentrations

Table 7 lists the ${\rm CO}_2$ concentration ranges of ${\rm CO}_2$ sources and control points including, the atmosphere, the ocean, and the industrial emitters including natural wells used for energy sources. The concentration of ${\rm CO}_2$ in the atmosphere and in the oceans are fairly constant around the globe. The concentration by weight in the atmosphere is about 5 times that in the ocean, however, because the ocean is about 1000 times denser than the atmosphere the total mass in a given volume in the ocean is about 200 times greater. The concentration of ${\rm CO}_2$ in industrial emissions are about ${\rm 10}^3$ to ${\rm 10}^4$ times greater than that in the atmosphere. Thus, the energy required to

proportional to the logarithm of the volumetric source concentration, so that theoretically it should take 3 to 5 times more energy to extract CO_2 from the atmosphere than from stacks of fossil fueled plants. Because of other inefficiencies and frictional losses, the relative energy requirements increases much more than the logarithmic proportionality as the concentration of the source decreases.

Table 7

CO₂ CONCENTRATIONS AT CONTROL POINTS AND MINIMUM

CO₂ SEPARATION ENERGIES

Control Point	CO, Concer	tration	Min. Separation Energy	
	% by Vol.	% by Wt.	kwh/1b CO ₂	

Atmosphere	331×10 ⁻⁴	502×10 ⁻⁴	0.0570	
Ocean	66x10 ⁻⁴	100×10^{-4}	0.0570	
Industrial Emitters				
Fossil Fueled Power Plants	7-20	11-28	0.0259-0.0179	
Chemical Plants (lime, cement, NH ₃ , coal gasif.)	20-100	28-100	0.0179-0.000	
Metallurgical Plants (blast furnaces)	20	28	0.0179	
Natural Gas Wells	0-50	0-73	0.0099	
Geothermal Wells	∿50	∿ 66	0.0099	

^{*}Minimum Energy based on free energy of mixing:

 $\Delta F = RT\Sigma n_i ln \frac{P_i}{P_i p}$, where P_i^o and P_i^o are the initial and final partial pressures of the i^{th} species, respectively. R is the gas constant, T is temperature in degrees absolute and n_i^o is the number of moles of the i^{th} species.

CO2 Removal and Recovery Processes

a) The atmospheric and oceanic control points

Taking the atmosphere as the ${\rm CO}_2$ control point one can estimate the amount of energy needed to remove and recover ${\rm CO}_2$. This has been done in a previous study for a number of options. Results are summarized in Table 8.

Table 8 ENERGY REQUIRED TO REMOVE AND RECOVER CO2 FROM THE ATMOSPHERE AND SEA WATER 6

		Energy for CO ₂ Separation
CO.	Removal and Recovery Process	kwh(e)/1b CO ₂
2		
1.	H ₂ 0 absorption/stripping (atm. pressure)	1.0
2.	H ₂ ⁰ absorption/stripping (20 atm)	9.7
3.	Methanol adsorption/stripping (20 atm and -80°F)	7.3
4.	Aqueous K ₂ CO ₃ absorption/stripping (atm pressure)	0.4
5.	CO ₂ adsorption/desorption	6.1
6.	Cryogenic Separation	9.2
7.	Caustic absorption/electrolytic strip (isothermal process)	ping 0.9
8.	Stripping of sea water	0.4

Note: For a bituminous coal burning power plant supplying power for for removal of ${\rm CO}_2$ in system 4 (aq. ${\rm K}_2{\rm CO}_3$), ${\rm CO}_2$ generated/ ${\rm CO}_2$ removed = 0.4/0.56 = 0.71 and net ${\rm CO}_2$ reduction/ ${\rm CO}_2$ removed = 1-0.71 = 0.29. At 100% ${\rm CO}_2$ removal efficiency, net power plant efficiency would be reduced from 38% to 10%.

The most energy economic system is the dilute aqueous alkaline K_2CO_3 system at atmospheric pressure because it has considerably higher solubility for CO_2 than water. An advanced isothermal system is also estimated using electrolytic decomposition of a carbonate-bicarbonate solution to release CO_2 and regenerate the alkaline carbonate solution to scrub the atmospheric CO_2 . The seawater stripping system has a low energy requirement because seawater

produced for a fossil fueled plant from Table 6, with the energy required to recover the $\rm CO_2$ shown in Table 8 one can estimate the ratio of $\rm CO_2$ produced to $\rm CO_2$ recovered. Thus, for all the processes listed in Table 8, with the exception of the aqueous $\rm K_2CO_3$ scrubbing and seawater stripping, more $\rm CO_2$ would be generated than recovered if a coal burning power plant were used to supply the electrical power. However, even in the $\rm K_2CO_3$ scrubbing case there is a significant penalty in energy generation efficiency. The conclusion to be reached here is that only a non-fossil fueled power plant such as nuclear or solar is allowable to generate the necessary electrical power for removal of $\rm CO_2$, from the atmospheric and ocean control points.

b) The industrial control points

For the more concentrated industrial emission streams, less energy is required to recover the CO_2 . Therefore, there is a larger margin for net CO_2 recovery if fossil fuel is used to power the CO_2 separation processes. However, estimates of energy requirements shown in Table 9 indicate that only for the high capacity solvent absorption/stripping processes (i.e. K_2CO_3 , MEA, caustic scrub) are the energy requirements low enough to allow fossil fuel power plants to supply power for the separation process. However, even use of these high capacity solvents will tend to reduce power plant efficiency as indicated in note (3) of Table 9.

Disposal of CO2

The removal and recovery of ${\rm CO}_2$ is only the first step in the environmental control chain. Disposal is probably the most critical step. Tables 5A through 5E lists a number of disposal schemes. The disposal breaks down into several ultimate possibilities.

1. Burial in the deep ocean

In the two-box model, the world ocean is represented by two reservoirs, separated by a thermocline. One reservoir consists of surface layers to a depth of about 100 meters; the other, of deeper layers from the 100 meter depth to the ocean floor. Mixing is assumed to occur rapidly within each box or reservoir, but exchange between the two boxes proceeds slowly. Thus, the deep ocean represents a sink for CO2 since there is no direct exchange between the atmosphere and the deep ocean. The main discrepancy between the simple two-box model and the real ocean is that in some regions (e.g. Artic, Antartic and Gibraltar regions) convection currents extend from the ocean surface to the ocean bottom.

One proposal for disposing of collected CO_2 is to inject it into the sea at the Strait of Gibraltar. Presumably, the current would carry it to the deeper ocean waters where it would remain for centuries. Another proposal is to inject liquid CO_2 into the deep sea at a density greater than that of deep sea water via a long pipe. The CO_2 would sink to the bottom of the ocean forming a liquid CO_2 lake within the ocean.

Energy for CO₂ Separations

CO₂ Removal and Recovery Process kwh(e)/lb CO₂

1. Aqueous K₂CO₃ absorption/stripping

2. Caustic absorption/electrolytic stripping

(isothermal process)

3. Amine absorption/stripping

4. Adsorption/desorption on molecular sieves

O.6

1.8

0.6(1)

Note:

Cryogenic Separation

Absorption in sea water (1)

- (1) 060% CO, removal efficiency and including deep ocean disposal of captured CO,
- (2) For coal burning plant energy output per unit ${\rm CO}_2$ generated is 0.56 kwh(e)/lb ${\rm CO}_2$; any removal system requiring values equal to or greater than this yields no reduction in net ${\rm CO}_2$ emitted.
- (3) For a K₂CO₃ removal system (process 1), the overall power plant efficiency would be affected as follows:

Lb CO ₂ Discharged To Atmosphere Per Net kwh(e) Generated
0
0.33
0.52
0.82
1.01
1.44
1.83

The current release rate of fossil carbon to the atmosphere is about 5×10^{15} g/yr, whereas the current carbon content of the deep ocean is estimated at 0.373 x 10^{20} g. Therefore, if all of this fossil carbon was collected and deposited in the deep ocean, the quantity of carbon contained therein would increase by about 0.013% per year.

by equilibrating a high CO_2 concentration on natural zeolite, is of main concern with this method of disposal.

3. Extraterrestrial burial

 ${\rm CO}_2$ packaged as solid, liquid or high pressure gas would be sent by rocket beyond the escape velocity of the earth or possibly to other planets. In this way one can assure that the ${\rm CO}_2$ would not gravitate back to earth. If non-fossil generated hydrogen is used as rocket fuel no exhaust ${\rm CO}_2$ penalty would be incurred, however, energy costs would be excessive.

4. Recycle in products

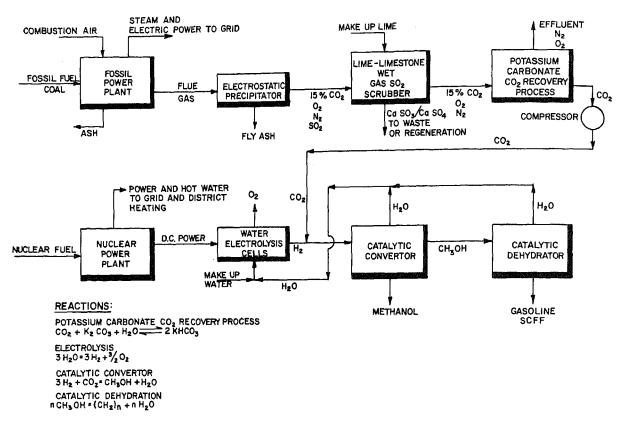
Although a number of ${\rm CO}_2$ containing commercial products can be made for the economy, i.e. dry ice, soda ash, inorganic carbonates, urea, the ${\rm CO}_2$ remains about the same because fossil energy is used to produce them and the markets for the products are limited.

A unique disposal method is to convert the recovered ${\rm CO_2}$ to synthetic liquid and gaseous carbonaceous fuel using a non-fossil energy source, for example, nuclear power. In this way, the ${\rm CO_2}$ can be reused thus reducing the ${\rm CO_2}$ buildup in the atmosphere. There are several options in applying this carbon-nuclear cycle. 8 , 9

- (a) Coal can be converted to SNG, oil, and gasoline using nuclear power based electrolytic hydrogen. The nuclear hydrogen would be used directly to hydrogenate the coal. In this manner the CO₂ buildup would be reduced by a factor of 3 compared to the natural gas and petroleum cases.
- (b) Remove and recover CO_2 from coal burning power plants and combine with nuclear electrolytic hydrogen to produce methanol which can be dehydrated to gasoline on zeolite catalysts. It Figure 3 shows a flowsheet of the system. In this manner, power is produced from the fossil plant and the carbon in the CO_2 reused in producing synthetic carbonaceous fuel.
- (c) Remove and recover CO_2 from the atmosphere and combine with electrolytically produced hydrogen to form synthetic carbonaceous fuels. A flowsheet of the system is shown in Figure 4 and features a novel isothermal (electrolytic) system for regenerating the CO_2 and caustic scrub solution in addition to the product hydrogen.

A quantitative estimate of the number of nuclear reactors needed to convert the $\rm CO_2$ emissions from industrial stack emissions to synthetic carbonaceous fuels for the transportation sector in the US is shown in Table 10. The data indicates that there is more than enough $\rm CO_2$ emitted from fossil energy power plants to supply the needs of the automotive industry and that about one thousand 1000 MW(e) nuclear reactors would be needed to make the total conversion.

21MILE IIC OVIVERINGERS



A potential large scale use for CO_2 is in tertiary treatment of depleted oil wells, however, this application may be of limited value as a long term disposal method. Another recycle system is to utilize the CO_2 as a diluent with oxygen in a fossil fuel power plant so that the only effluent is CO_2 thus reducing energy requirements for removal and recovery. With this system a compact highly efficient power plant can be designed. The plant can be sited in highly populated areas and the CO_2 removed for disposal in remote areas.

Finally, an all nuclear or solar-electric hydrogen economy would essentially reduce ${\rm CO}_2$ emissions to a negligible level.

FIXATION OF ATMOSPHERIC CARBON

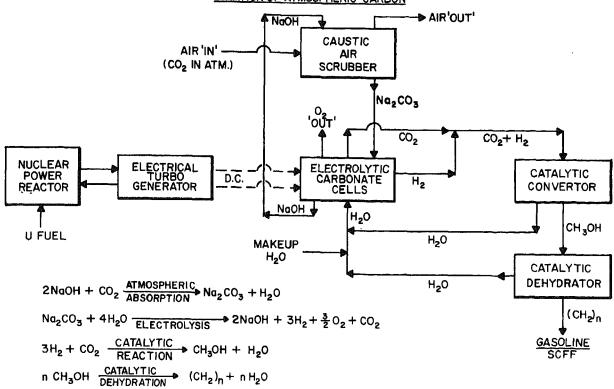


Table 10

INDUSTRY RESOURCE CAPACITY TO PRODUCE SYNTHETIC CARBONACEOUS FUELS AND FEEDSTOCKS FROM EFFLUENT CO AND ${
m CO}_2$ FEEDSTREAMS AND NUCLEAR POWER 9

Based on 1975 Production Capacities

Industry	Production capacity Millions tons/yr	CO ₂ or CO availability Millions tons/yr	Gasoline production capability Billions gal/yr	No. of 1000 MW(e) nuclear power plants required
Lime and Cement	25 Lime 85 Cement	86 c0 ₂	9	90
Stee1	125 Stee1	125 CO	20	125
Coal for Power	500 Coal	1,560 c0 ₂	165	1,680
Gasoline, US Consumption		(945 c ₀ 2) (1	100	(1,000)(1

¹⁾ Capacity needed to meet 1975 US consumption of gasoline of approximately 100 billion gal/yr.

measures can be recommended.

- (1) Attempt to find and utilize more natural gas (and petroleum) in preference to coal because of its 2 to 3 times lower CO₂ emissions per unit energy produced.
- (2) Consider recovering the more concentrated ${\rm CO}_2$ industrial stack gas emissions using fossil fuel power.
- (3) Attempt recovering the less concentrated atmospheric and oceanic ${\rm CO}_2$ using nuclear power or another non-fossil power source such as solar.
 - (4) Consider disposal of the CO_2 by deep ocean burial.
 - (5) Combine coal with nuclear electrolytic hydrogen to produce SNG.
- (6) Produce synthetic carbonaceous fuel from atmospheric ${\rm CO}_2$ and nuclear electrolytic hydrogen.
 - (7) Convert to a hydrogen economy using a non-fossil energy source.
- (8) Convert to an all electrical economy substituting nuclear or another non-fossil fuel source such as solar.
 - (9) Convert to a biomass photosynthetic energy economy.

Since no energy source is truly benign, in the long run, the realistic ECT scenario for ${\rm CO}_2$ will depend on the lesser of the evils in selecting and utilizing our energy source alternatives.

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1. INTRODUCTION

If we burn fossil fuels at too rapid a rate in the future, there is a real threat of unacceptable consequences from increasing levels of atmospheric carbon dioxide. While the uncertainties involved are large, there are ample reasons for concern:

Atmospheric carbon dioxide is increasing.

The rate of fossil fuel consumption has increased exponentially for 120 years.

The reserves of fossil carbon are very large.

The oceans can take up carbon dioxide from the atmosphere at only a limited rate.

The magnitude of the greenhouse effect may be several degrees Celsius per doubling of atmospheric carbon dioxide.

If we do not limit the rate of fossil fuel consumption in the future, it seems essential to consider, as Dr. Steinberg has outlined in his paper, possible means of controlling the excess carbon dioxide produced.

The goal of our study, which is still underway, has been to examine in more detail the technical feasibility, monetary cost and energy cost of some of the more promising means of capture and disposal. Specifically we have restricted ourselves to the collection of carbon dioxide from stationary sources such as power plants, though these amount to only 20 to 30% of the total fossil carbon dioxide flux, and the only means of disposal we have considered in any detail is ocean disposal.

^{*}Research sponsored by the Division of Environmental Control Technology, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

gas by present technology have been estimated by Pappano et al. (1976) and by Rump et al. (1977) for large scale operations (in the later case, 270 metric tons of CO₂/hr) for enhanced oil recovery. In Table I, these energy costs are compared with the energy worth of the carbon dioxide, i.e., the energy derived by burning the coal that produced it. We have assumed a coal (Sewanee Coal from Grundy Co., Tenn.), one metric ton of which produces 6.79 million kcal of heat and 2.55 metric tons of carbon dioxide. This gives a cost of CO₂ recovery that is about 46% of the energy worth. The dollar cost is estimated at about \$19 per metric ton of CO₂ (\$1.80/million BTU).

The estimated energy cost of compression to 150 atm and transporting 25 miles are small by comparison. The estimated energy costs of conversion into solid forms such as dry ice or the hydrate are more appreciable, 14 to 18% of the energy worth of the carbon dioxide. The dollar costs of these steps are proportionately higher because much of the energy consumed is electrical.

TABLE I. COST OF COLLECTING AND PROCESSING CO, FROM STACK GAS

	10 ⁶ kcal Metric Ton of CO ₂	% of CO2 ^b Energy Worth	\$/Metric Ton of CO ₂
Capture of ${\rm CO_2}^{lpha}$	1.23	46	19
Compress to 150 atm, α Transport 40 km	0.10	4	4
Solidify ${\rm CO_2}^c$			
To Dry Ice	0.36	14	14
то со ₂ ∙6н ₂ о	0.47	18	17

 $[\]alpha$ Rump et al. (1977). 290 metric tons CO_2/hr , MEA process.

COMBUSTION IN OXYGEN

Marchetti (1978) has suggested that coal be burned in pure oxygen to produce nearly pure carbon dioxide and water, thus avoiding the costly collection from flue gas. Table II summarizes the comparable costs of this alternative.

^bOne metric ton of coal assumed to yield $6.79 \cdot 10^6$ kcal and 2.55 metric tons of co_2 .

 $^{^{\}it c}$ Calculated from data of Stickney (1932).

Preparation of Pure Oxygen α (22 atm)	0.76	29
Increase in Plant Efficiency (38% to 42%)	<u>-0.28</u>	<u>-11</u>
Net Cost	0.48	18
Capture CO ₂ From Stack Gas	1.23	46

aFrom data supplied by P. Koster, Linde Div., Union Carbide Corp.

The major cost is, of course, the separation and compression of oxygen from air, amounting to 400 kWh of mostly electrical energy per metric ton of oxygen. Since 2.15 metric tons of oxygen are required to burn one metric ton of our coal, this amounts to 1.95 million kcal/metric ton of coal (assuming 38% efficiency for the production of the electricity). Thus the oxygen production costs amount to 0.76 million kcal/metric ton of $\rm CO_2$, considerably less than the cost of recovering $\rm CO_2$ from normal flue gas.

Moreover, it is reasonable to expect there will be an increase in plant efficiency from (1) the reduction in heat loss to the stack gas, (2) the elimination of the combustion air fans, (3) perhaps an increase in combustion temperature. If an improvement in overall efficiency from 38% to 42% were possible, this would amount to 0.28 million kcal/metric ton of CO which could be credited against the production costs of the oxygen.

An additional possible advantage of combustion in pure oxygen is that there may be no need for an $\rm SO_2$ scrubbing step which otherwise would precede the $\rm CO_2$ scrubber. The $\rm CO_2$ and $\rm SO_2$ could be compressed and disposed of together.

4. OCEAN DISPOSAL

If carbon dioxide can be delivered to the deep oceans this would give a retention time of the order of a thousand years even if this acidic gas did not react with the basic minerals present such as calcium carbonate. We will consider various forms of carbon dioxide that would be denser than seawater and have a vapor pressure lower than the hydrostatic pressure at the depth of injection.

increases the density. The apparent molar volume of dissolved $\rm CO_2$ (measured before the turn of this century and cited by Eley, 1939) is about 35 cm³. The density increase at the maximum solubility is only about 1%, however, not enough to exceed the density of seawater. Hence fresh water does not seem suitable as a medium for the disposal of carbon dioxide in the ocean.

TABLE III. THE CO₂ CONTENT AND DENSITY OF WATER AT THE LIQUEFACTION PRESSURE OF CO₂

Temp.	Vapor Pres. of Liq. ${^{ m CO}_2}^{lpha}$	Dissolved $C0_2^b$ (Moles/kg H_2^0)	Conc. ^b (Wt %)	$\frac{\rho (Sol'n)^{\mathcal{C}}}{\rho (H_2O)}$
0	34.4	1.45	6.02	1.0125
5	39.1	1.36	5.64	1.0117
10	44.4	1.29	5.37	1.0111
15	50.2	1.25	5.22	1.0108
20	56.5	1.24	5.16	1.0106
25	63.5	1.25	5.22	1.0108
30	71.2	1.29	5.39	1.0111

 $[\]alpha$ Vukalovich and Altunin (1968), p. 97.

4.2 Carbon Dioxide in Seawater

The solubility of carbon dioxide in seawater as a function of pressure up to the liquefaction pressure at various temperatures is shown in Fig. 1. Assuming conservatively that the molar volume is no larger in seawater than it is in fresh water, there should be a substantial density increase, for example, $0.0075~{\rm g/cm^3}$ at a concentration of 1 mole/kg. The minimum depth of injection without the formation of bubbles is shown on the upper scale.

To consider further the disposal of carbon dioxide in seawater, let us imagine the simple system shown in Fig. 2: Water is taken in at a temperature of t_1 and density ρ_1 which depend on the location and depth chosen; it is pumped through a gas-liquid contactor where CO_2 is dissolved to a concentration C, the density rises to ρ_3 and because of the heat of solution the temperature

 $^{^{}b}$ Based on data in Linke (1958), p. 460.

 $[^]c$ Calculated assuming the molar volume of dissolved CO $_2$ is 35 cm 3 .

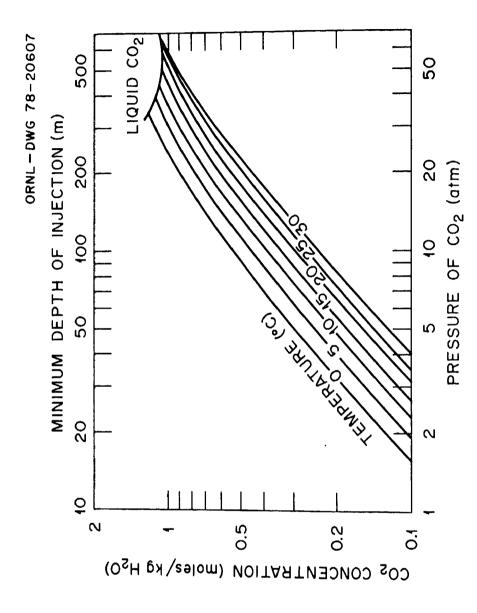


Fig. 1. Solubility of CO₂ in Seawater

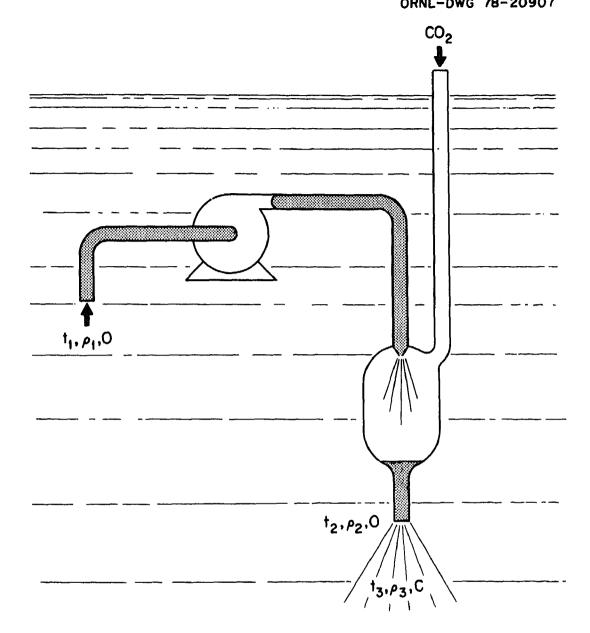


Fig. 2. Schematic Representation of the Injection of ${\rm CO}_2$ into Seawater

ic composaves 5

$$t_3 = t_1 + 5 \cdot C , \qquad (1)$$

based on a heat of solution of 5 kcal/mole. The density difference at the outlet, $\rho_3-\rho_2$, can be calculated as the sum of two terms.

$$\rho_3 - \rho_2 = [\rho(t_3, 0) - \rho(t_2, 0)] + [\rho(t_3, 0) - \rho(t_3, 0)]. \tag{2}$$

The first is the density decrease caused by heating the ambient seawater from t_2 to t_3 , known accurately from data for seawater. The second term is the density increase produced by introducing the carbon dioxide to a concentration of C moles/kg, and can be estimated from the approximation

$$\rho(t_3,C) - \rho(t_3,0) \stackrel{\circ}{=} 0.0072 \cdot C$$
, (3)

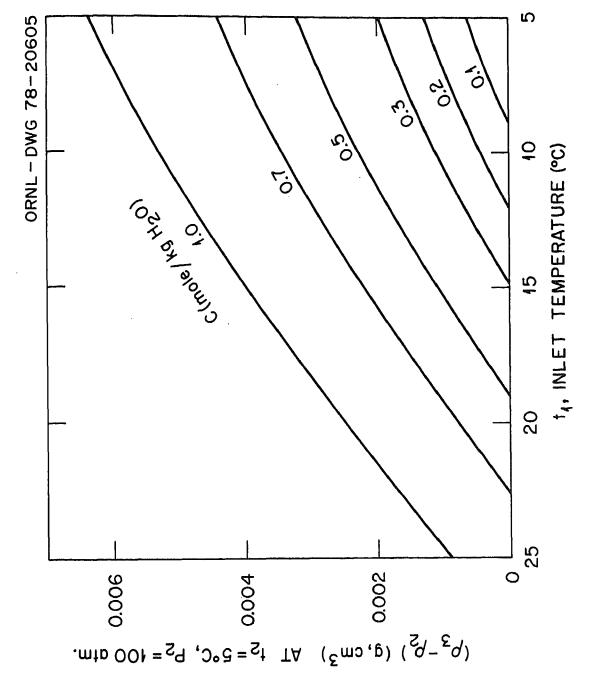
based on a molar volume of 35 cm³.

It turns out that the density difference, $\rho_3-\rho_2$, which we wish to maximize depends on two quantities, the inlet temperature t_1 (which should be minimized) and the concentration of carbon dioxide C (which should be maximized). The calculations plotted in Fig. 3 were done assuming the injection point was at the bottom of the thermocline (\sim 1,000 m depth) where the water temperature becomes approximately constant below 5°C. Injection at lesser depth would give larger density differences because the ambient water temperature is higher.

One of our early ideas for the disposal of carbon dioxide from a coalfired power plant was to take advantage of the cooling-seawater requirements of an ocean thermal energy conversion (OTEC) plant. A 1,000 MW(e) coal-fired plant produces about 210 kg/sec of carbon dioxide. If this were dissolved in seawater to a concentration of 0.5 moles/kg, about 10,000 kg/sec of water flow would be required. A 100 MW(e) OTEC plant proposed by TRW Inc. would require 380,000 kg/sec of cooling water. This is 38 times the flow rate required to dissolve the CO2 released by a 1,000 MW(e) fossil fuel plant, and we thus conclude that there would be no advantage in using the OTEC plant. The same benefit could be gained by siting the fossil plant on a floating platform or at a coastal location where the CO2-seawater solution could be discharged at the proper depth. Indeed the seawater requirements for such disposal are so modest that if deep ocean water were used for cooling the condenser of a coal-fired plant, it could carry away all the carbon dioxide produced by the plant at a concentration of the order of 0.1 moles/kg while at the same time offering greater thermal efficiency because of its lower temperature.

4.3 Carbon Dioxide Hydrate

The hydrate of carbon dioxide has a clathrate structure (Miller and Smythe, 1970) with a density of about $1.12~\rm g/cm^3$, greater than that of seawater. If large blocks of the solid were dropped into the sea they would sink rapidly.



The Excess Density of a ${\rm CO}_2$ Disposal Stream in Seawater Fig. 3.

formation would cease. The reaction product thereafter would be a carbon dioxide-seawater solution more dense than the surrounding water. The reaction rate might be slow enough to permit the block to reach the bottom before an appreciable fraction had been consumed.

4.4 Liquid Carbon Dioxide

Marchetti (1976) has mentioned a suggestion of Nordhaus for disposal in the form of liquid carbon dioxide. In Fig. 5 we see that while the density of the liquid is less than that of seawater at the surface, it is much more compressible and has a much higher thermal coefficient of density. From these curves it appears, however, that a considerable depth of injection would be necessary, about 3,000 meters, to insure that the CO₂ is more dense than the surrounding seawater.

4.5 Dry Ice

This form has the greatest density, about $1.5~\rm g/cm^3$, and would be the most economical to transport by water. Large blocks of it would sink rapidly and, again, once past a depth of about 500 m, bubbling should cease and the reaction products - the hydrate, the liquid and dissolved $\rm CO_2$ - should be denser than the surrounding water. This form of carbon dioxide might survive the trip to the ocean bottom best of all.

5. SUMMARY AND CONCLUSION

- 1. The cost of ${\rm CO}_2$ recovery from flue gas will be high.
- 2. Combustion of fuel in pure oxygen may permit a more efficient recovery of ${\rm CO}_2$ (and ${\rm SO}_2$).
- 3. Deep ocean disposal would give a long retention time.
- 4. Fresh water is not a suitable medium for ocean disposal.
- 5. Seawater could be used because dissolving ${\rm CO}_2$ should increase the density of seawater.
- 6. The cooling water flow from one OTEC plant could accommodate the ${\rm CO}_2$ output of hundreds of fossil fuel plants of the same capacity.
- 7. The cooling water flow from a fossil fuel plant is more than adequate to accommodate the $\rm CO_2$ output of the plant, but the plant must be sited to permit ocean disposal.
- 8. We need more data on the density effect of introducing ${\rm CO}_2$ into seawater as a function of temperature and pressure.

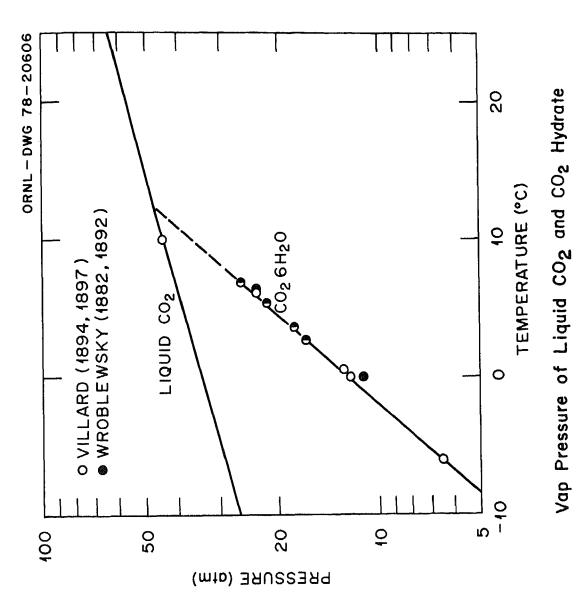
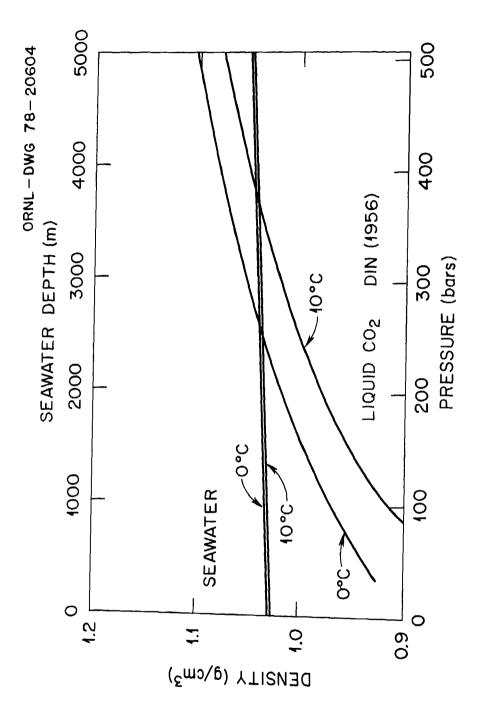


Fig. 4. Vapor Pressure of Liquid ${\rm CO}_2$ and ${\rm CO}_2$ hydrate. Data Cited by Quinn and Jones (1936)



A Comparison of the Densities of Liquid ${
m CO}_2$ and Seawater Fig. 5.

ice.

11. Liquid CO_2 might be used for ocean disposal, but the depth of injection would be over 3,000 m.

ACKNOWLEDGMENT

This study is being funded by the Department of Energy's Division of Environmental Control Technology, through the Office of Fred Witmer. We gratefully acknowledge the contributions of Ralph Rotty of the Institute for Energy Analysis and of William Fulkerson and Garland Samuels of ORNL's Energy Division.

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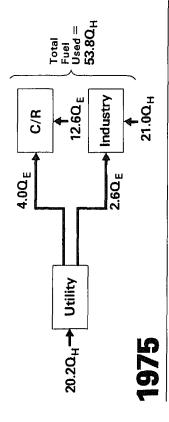
Energy Technology Fossil Fuel Utilization

Cogeneration is classicly thought of as a conservation technique. What is perhaps less appreciated is the fact that cogeneration is also a technique for the reduction of emissions. This is one of the benefits of a cogeneration system since less fuel is burned to produce electrical power and process heat than in isolated powerplants or furnaces. Despite these benefits. there is concern that if cogeneration becomes widespread in the US on the scarce fuels of today (natural gas and light distilate petroleum) it could potentially displace the coal required by utility power generation and increases our imports of scarce fuels. If that can forseeably happen, and the US balance of payments to foreign countries were to increase, then very reasonable arguments can be made that cogeneration should not proceed without regard for the systems' potential for switching to fuels from far more abundant sources-like coal and coal-derived fuels. The author's position is not necessarily one of announcement of DOE policy but it is very much one of advocacy for cogeneration and the development of engine technology that can operate reliably and cleanly on fuels from coal at dispersed sites with the potential for utility ownership. Very direct benefits that this will permit are (1) the reduction of national consumption of scarce petroleum and natural gas to help the US balance of payments problem, (2) big increases in national coal production requirements, and (3) reduction in the amount of fuel required to make both electricity and process heat by factors ranging from 20 to 40% for the purposes of emission reductions on minimally processed coal-derived fuels, (4) keeping the cost for fuel burned in an operation from rising due to increased costs/BTU on coal-derived fuels and (5) dispersed power generation should reduce national vulnerbility to disaster of one form or another.

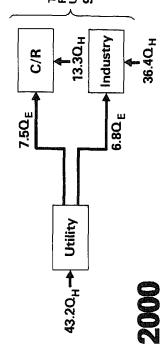
To give the reader some indication of how large the opportunity is for coal in cogeneration systems to meet the country's growing electrical and heat demands, refer to Figure 1. This shows a current and projected schematic of how energy is used in our two stationary sectors (commerical/residential and industrial) and how it is supplied by the purchase of fuel and the purchase of electricity from a utility company. In the year 2000, a projection of how heat and electrical requirements might be met with and without cogeneration is shown. Cogeneration is shown in the schematic to be used to meet national electricity growth requirements of nearly 8 quads electric between 1975 and 2000, with some recovered on-site waste engine heat being used to displace fuel that would otherwise be burned for process heat in these two sectors. While the overall national energy savings are only 5.3 quads/year, the new market for fuel burned in engines in cogeneration systems in this upper bound scenario is 25.3 quads/year. If heat engines and fuels from coal can be developed to meet this market and it's constraints (technical, environmental and cost) then this can be considered as a market for coal rather than scarce fuels. Note that this 25.3 quad/year market by 2000 is in addition to the current 20.2 quad/year fuel requirement of utilities.

The Opportunities for Coal Cogeneration in the New Market - Year 2000

No Cogeneration



No Cogeneration



Symbols and Notes

 $\Omega_{H} = \Omega uads$ Fuel Burned/Year

Q_{WH}=Quads Waste Heat Recovered in Cogen/Year

O_E = Quads Electricity Made/Year

- 33=Utility Electric Generation Efficiency
- 30=Cogen Site Electric Generation Efficiency
- 60=Total Cogen Cite Site Conversion Efficiency

11.50_H C/R Site 3.40_{WH} 20.20_H Utility 13.80_H 10.60_E 10.40_E 10.

Gas Turbine - HRSG Cogeneration Characteristics Figure 2.

..... Air Cooled 1750 F PR = 10

----- Air Cooled 2200 F PR = 12

Water Cooled 2800 F PR = 16

100 TSOURCE (°F) = TSTACK 8 . Heretely treetely Fuel Saved/ Fuel Burned 1.0 0.2 0.8 9 0.4 → STACK — HRSG D POWER ₩ TSOURCE (°F)=TSTACK 88 400 28 ¥ ₽ Heat/Fuel Power or 1.0 0.6 Ratios 0.8 0.4 -

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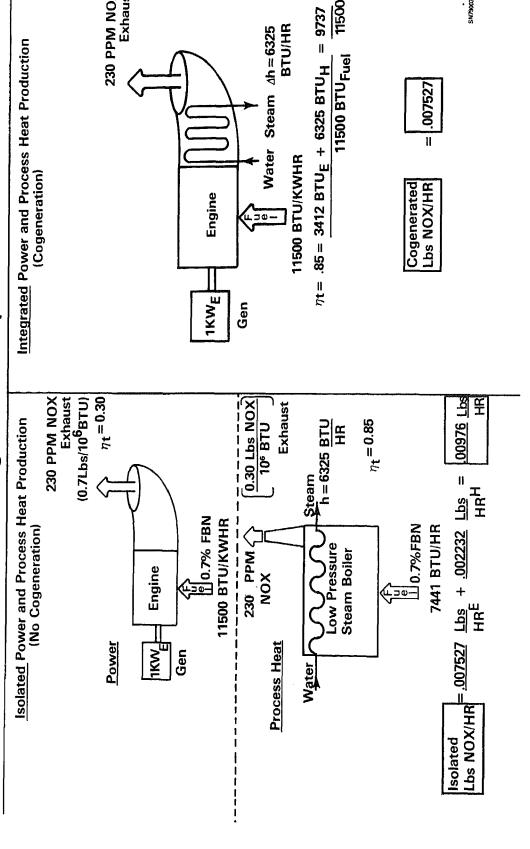
A very major technical barrier confronting the successful substitution of coal for scarce fuels is the fact the emissions from the combustion of coal derived fuels can be high enough to be considered unhealthy. The two most obvious solutions in engines are to (1) clean up the fuel to remove the polutants or (2) to develop engine technology to either burn more cleanly or clean up the exhaust products. A third solution, which is not quite so obvious is also applicable in reducing emissions. This third solution is cogeneration - the simultaneous generation of electrical or shaft power and process heat. The technical key to understanding how cogeneration can reduce emissions lies in understanding that in a "topping" type cogeneration system, the waste heat from a powerplant is used to make process heat instead of firing up an isolated furnace. The emission reduction comes from the industrial or commercial/residential furnace that is no longer lit. These 2 sectors now consume about 7 quads of electricity and 34 quads of fuel for heat, mostly in isolated non-cogenerated installations. In the future these requirements may be even greater and come to us at a time when it would be most desirable to meet these requirements using our most abundant fuel - coal. Means to do this job without sacrificing our environment however, are badly needed. Within these constraints it appears that cogeneration can be one of the most promising ways to make the combustion of coal acceptable for both power and process heat generation. The solution which this paper offers, cogeneration, not only reduces emissions it also is highly fuel efficient and can provide a market for the more economic, minimally processed coal-derived fuels. Some of the technical reasons why coal-derived fuels are not being used this way today even on a trial basis, are that (1) the best* of today's engines for cogeneration (diesels and gas turbines) can have severe operating problems on the impurities in these fuels. (2) even the emission reductions possible through only cogeneration are not enough to meet proposed EPA engine standards and (3) critical technologies for the balance of the coal cogeneration plant beyond the engine have not been investigated enough to know what their problems and solutions are. If these problems can be solved, there is still some barrier potential for industrial or commercial/residential cogeneration that can be anticipated if the environmental standards are based upon emissions per BTU input rather than emissions per usefull BTU output. In a cogeneration system, the usefull output can be on the order of 3 times higher than that of an isolated non-cogenerated powerplant with no increase in site emissions, despite the very large increase in usefull energy conversion. It seems very reasonable to the author that an environmental credit should be given for this added capability in BTU or equivalent KWHR that cogeneration can provide.

The following develops the rationale for these claims of emission reduction and increased useful output. Refer to Figures 2 to 5. Figure 2 from Reference 1 shows a candidate open cycle gas turbine cogeneration scheme making both electricity from a shaft driven generator and low temperature

*1) Best here means highest power/heat ratio.

Effect of Cogeneration Upon Emissions

Exhau



11500

. 50087NS

Taking Credit For Cogeneration Benefits On .7% FBN Coal Liquid

Figure 4.

MAMO Useful

Slashed By Emissions Engine Emissions/Output - Isolated = .00753/3412 = 2.85 1. If All The Credits Are Given To The Engine: Aiples!
Engine Emissions/Outnut '--' .00753/9737 Engine Emissions/Output - Cogen

2. If All The Credits Are Given To The Cogen System: Over 20%!!

= .00753Total Plant NOX - Isolated Total Plant NOX - Cogen

Isolated Equivalency

Emits Like FBN Was Only .3%! 92600

\$.80|10° BTU! Saves \$.10 to Engine - 230 ppm NOX \times .77 = 177 ppm

Boiler - .30 lbs NOX \times .77 = .23 lbs NOX 10^6 BTU lnput 10^6 BTU B

Desired Standard!!! Better Than EPA

now comes from the cogeneration system.

For a direct comparison of emission and fuel reductions between isolated and cogenerated power and process heat generation on coal-derived fuels, see Figure 3. This figure shows an isolated boiler making low pressure process steam and an isolated gas turbine making electrical power. For illustration and comparison purposes, the boiler is sized to put as many BTU/HR into steam as the cogenerated gas turbine does. To make the case scaleable, the electricity generated is 1 KW. In the illustration, the fuel used is an undefined coal-derived liquid containing .7% fuel bound nitrogen with both the boiler and the turbine using the same fuel. The fuel bound nitrogen level selected corresponds closely to that of fuels that were burned in a gas turbine combustor (Ref. 2) and in a utility furnace that had originally been sized for coal (Ref. 3 and 4). The engine and boiler emissions of NOX shown in Figure 3 are therefore, based upon actual coalderived liquid fuel burns in production equipment. No speculation is made in this paper as to whether or not these values are going to be typical, but the ones shown do reflect what was measured. Cogeneration is shown to reduce the system emissions of NOX by 23% owing to the elimination of the boiler, its fuel demand and the emissions from that fuel. This brings up a subtle but very important point, that any impact of cogeneration is due to the equipment it replaces. The boiler shown in the example only emitted .3 lbs ${\rm NO_X/10^6}$ BTU fuel input. If, for whatever reason, that emission had been higher, say .7, as might occur on furnaces originally designed for natural gas or light distillate, then the lbs of NO,/Hr would have risen from .00223 to .00521 for the boiler contribution. This would have raised total system emissions of NO_x/Hr from .00976 to .01274. Eliminating such a high emission boiler through cogeneration would reduce total emissions by 41%. The point is that the impact of cogeneration upon emissions is dependant upon what is being replaced.

Figure 4 shows some various aspects of how these emissions reductions might be credited for the user. Two methods are shown. The first method credits the emission reduction uniformly for all members of the system as a whole -rather than to one component of it. In this form of acreditation, the total NOX reduction for power and process heat production is 23%. This means that the site of the cogeneration system is only making 77% of the NOX that would be formed by an isolated gas turbine plus an isolated boiler. For the boiler this would be equivalent to an isolated unit emitting only .23 lbs $\rm NO_{\rm X}/10^6$ BTU, which is considerably better than EPA standards. For the gas turbine, a 23% reduction in NOX would be equivalent to reducing its

*1) Ref. 1 also shows a combined cycle gas turbine (42% efficiency) with its waste steam going directly to process heat with 70% cogeneration system efficiency in the 300° - 400° F stack temperature range.

is worth noting that based upon Ref. 2's information, a reduction in NOX from 230 ppm to 177 ppm is equivalent to operating an isolated engine on .3% FBN fuel rather than .7% FBN. In a system that combined both cogeneration and an advanced low NOX combustor gas turbine, the minimally processed .7% FBN fuel might have been used and the additional fuel cleanup cost avoided. Over a 5 year period, operating 65% of the time (28470 hrs), a fuel cost savings (by being able to use .7% FBN instead of .3% FBN fuel) of \$.60/MBTU (Ref. 5) would result in a savings of \$196.40/KW. Since this figure is higher than the installed price of a gas turbine, it suggests that just the savings in not having to do additional fuel cleanup would pay for the powerplant in 4-5 years.

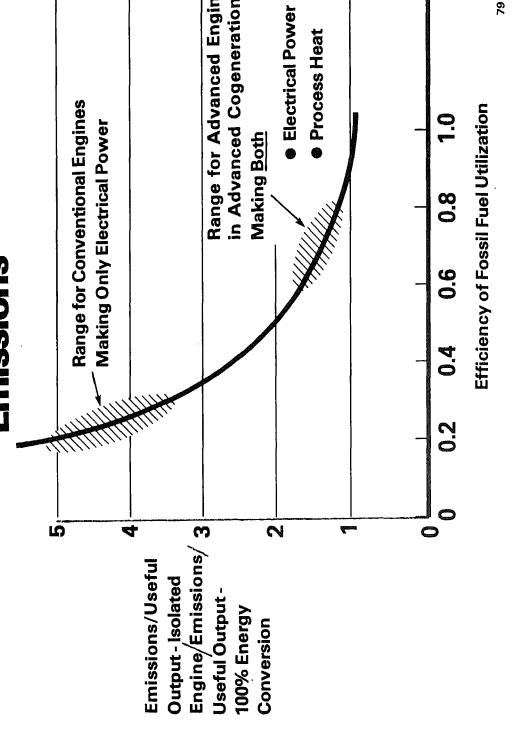
Compared to the isolated system, the cogeneration system only consumes 60% as much fuel for the same output. One way of interpretting this is that the cogeneration system could possibly more easily afford a substantial increase in fuel price if it were to rise from \$3/MBTU (today's price) up to \$5/MBTU (a possible future price).

In summary, the substantial impacts of cogeneration for the case given were:

- 1) An actual fuel consumption reduction of 40%, and an attendant NOX reduction of 23 to 41%, depending upon the performance of the replaced boiler.
- 2) An ability to burn minimally processed coal-derived fuels, rather than the more highly processed varieties with a savings over a 4 to 5 year period big enough to pay for the installed capital equipment price of even advanced gas turbine powerplants.
- 3) An ability to tolerate a rise in fuel price from \$3/MBTU up to \$5/MBTU if the fuel is used in a cogeneration system with no increase in price of either electricity or process heat to the customer because of a fuel price increase.

The second method gives all the credit to the engine due to the fact that although it's emissions do not change, its output in terms of useful BTU's goes up by a factor of 2.8. This output per emissions factor is simply the ratio of engine thermal efficiency with and without cogeneration. Usually this does not mean that emissions are reduced by a factor of 2.8. There are certain cases however, where it does mean exactly that. These are the cases where heat can be supplied in lieu of electricity for direct element heating, particularly where this electricity comes from peaking gas turbines. For the case given, if the cogenerated low pressure steam (or hot water) could replace electricity made by isolated gas turbines like the one in the example, the NOX produced to make the same useful output (9737 BTU) would be .00753 lbs, rather than (9737/3412)x .00753 or .0213 lbs, which is lower

The Impact of Advanced Cogeneration or **Emissions** Figure 5.



for this paper. However, some gross definition of the impact of cogeneration upon the emissions of the cycles is still desirable. An attempt to show this is given in Figure 5.

Figure 5 shows the ratio of emissions/output for isolated powerplants to emissions/output for 100% energy conversion plotted versus installed thermal efficiency. This curve is a direct presentation of the second method of acreditation given previously in which all the credit for the conversion to additional useful energy is given to the engine. The message from the figure is that cogeneration can boost the useful power and heat output of engines by factors as high as 3. While this does not reduce the site emission level for power generation, it does reduce the need for combustion of a fuel elsewhere to get the extra output now being made through cogeneration. In the example given, the ordinate value for the isolated gas turbine making only electrical power is 3.33 and the value for the cogenerated gas turbine is 1.18. The ratio of those two values is 2.8 which means the output of the cogenerated system is 2.8 times as much as the isolated system with no increase in fuel consumption or emissions.

The preceeding has given a reasonable indication that cogeneration can have a large beneficial effect not only in reducing emissions but also in making large financial savings in the life cycle of power and heat generation on minimally processed coal-derived fuels. Cogeneration seems to be a means of overcoming many of the technical, economic and environmental problems associated with coal. In recognition of such powerful leverage, in FY 1978 and FY 1979, the Fossil Energy Group of Energy Technology at DOE has established a series of major programs intended to (1) identify the major opportunities for cogeneration on coal and (2) to develop the technology in engines to permit them to operate reliably and cleanly on the lower cost minimally processed coal-derived liquid fuels.

In the first area, the 1985-2000 time frame is being addressed with major emphasis on obtaining optimum matches between engines of all types and the electrical and process heat requirements of 6 major industries and a commercial/residential mix. The industrial program now constitutes 2 major parallel study contracts (GE and UTC) let through NASA, Lewis Research Center. They are investigating the technical merits of diesel, stirlings, gas turbines, steam turbines, fuel cells, thermionics, bottoming cycles and energy storage for cogenerating the chemical, refining, paper, metals, stone/clay/glass/cement, and food industries with extensive applications of coal-derived fuels being sought. This program is called the "Cogeneration Technology Alternatives Study" (CTAS) and the contracts end in March 1979. The commercial/residential study is termed "Total Energy Technology Alternatives Study" (TETAS) which is being conducted in-house at Argonne National Laboratory. In this study, ANL is trying to find optimum matches between most of the topping cycles and heat pumps of CTAS and the power/heat requirements of a commercial/residential mix - shopping center, townhouses,

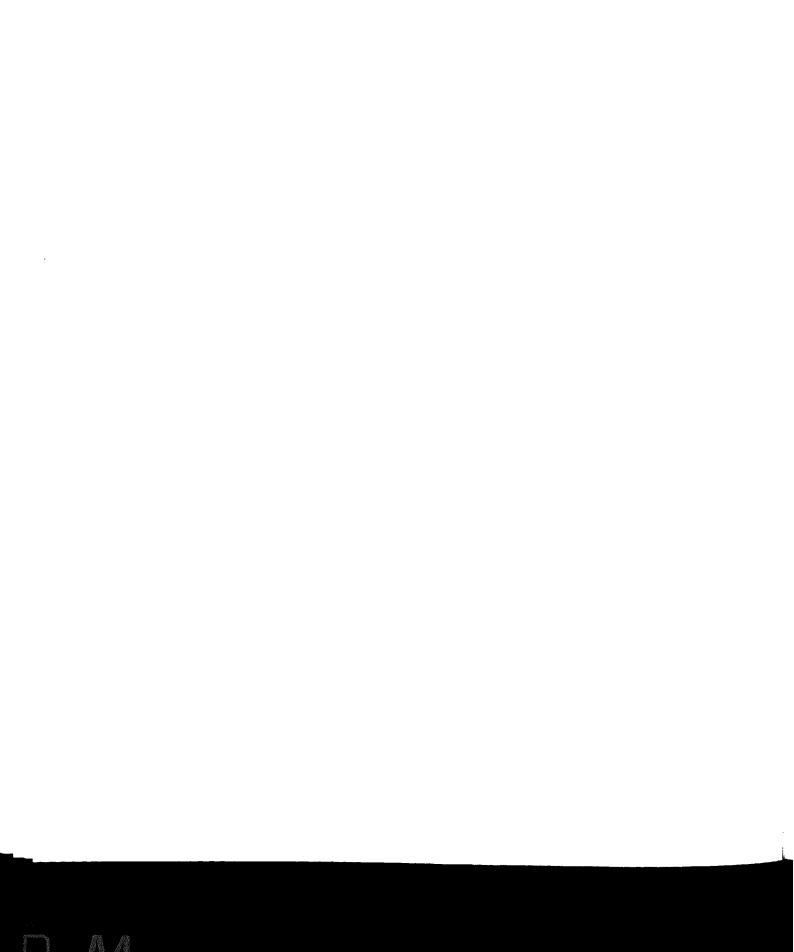
The one major assumption of the above studies is that they, by definition. presuppose that engines can operate at least reliably and possibly cleanly on coal-derived fuels. With the exception of the steam turbine, this is not necessarily true today. Fortunately, however, Fossil Energy in DOE has made major strides in establishing engine programs to provide the fuel flexibility capabilities that the studies assume exists. The major thrust of the programs are in diesels, gas turbines and Stirlings. The Stirling has the most fuel flexibility of all, because like the steam turbine it is externally fired which means its working fluid never comes into contact with the products of combustion. The Stirling's problem is that its major development for widespread commercialization was stopped around the turn of the 20th century due to the availability of cheap, clean, fuels suitable for internal combustion engines. Fossil Energy will have 2 small units built and scheduled for their first run in FY 1979. The conceptual design of a large unit will be started in FY 1979 with the first engine to test about 5 years later. The gas turbine can burn mostly any liquid or gas that is combustible, including coal-derived fuels. The gas turbine's problem on coal-derived fuels is that without additional processing of the fuel, many of these fuels contain traces of what is in coal - namely fuel bound nitrogen which produces high NOX levels, ash which may give turbine erosion problems and minute quantities of vanadium and alkali metals that give the turbine severe corrosion problems. The solutions to these problems seem to be the development of coatings and low-NOX combustor techniques. Two major DOE programs in these two technologies will be on multiple contract by January, 1979. With adequate funding, the programs will last about 5 years each and will be complete with demonstration in an engine(s). This work dovetails with complimentary development efforts on gas turbines for utility companies being performed through EPRI for baseload and intermediate capability on residual oils and coal-derived fuels. Of the three powerplant types mentioned, the one which seems closest today to a multi-fuel capability is the stationary diesel. This is based upon the fact that under DOE sponsorship several coal-derived liquid fuels have been run in a large diesel engine with less than a 10% increase in NOX as compared to light distillate operation. DOE plans to initiate a program in FY 1979 that will more fully asses a range of stationary diesel sizes on coal-derived liquid fuels. The primary things to be learned relate to emissions, corrosion, erosion, deposition, wear and what it takes to get fuels with very low cetane numbers to ignite.

The overall conclusion of this paper is that cogeneration offers a very powerful technique for the successful use of coal as a means of reducing oil imports, emissions, fuel costs and operating costs. The key technologies will require continued development in three major complimentary areas — coal-derived fuel processing, engines to burn these fuels cleanly and reliably and all other critical components needed to cogenerate besides engines and fuels.

Schenectedy, NY 12345

2. Efforts performed in 1978 under "Combustors for Coal-Derived Liquids With High Bound Nitrogen," EPRI Contract RP 989-1, by Westinghouse Electric Corp., Lester PA 19113

- 3. Mr. Richard Corey, DOE/ET/FE, Oct. 1978, 20 Mass. Ave. N.W., Washington, D.C. 20545
- 4. Mr. Don Teixeira, Oct. 1978, EPRI, 3412 Hillview Avenue, P.O. Box 10412, Palo Alto, CA 94303
- 5. "Economic Screening Evaluation of Upgrading Coal-Liquids to Turbine Fuels" AF-710, Technical Planning Study 76-666, Final Report March 1978, by Mobil Research and Development Corp., Billings Port Road, Paulsboro NJ 08066, EPRI Project RP 361-2



FOSSIL FUELS — ADVANCED METHODS I (LIQUIDS)

Chairman: William Peters

Co-Chairman: Fred Witmer

C. E. Schmidt and M. S. Edmunds U.S. Department of Energy Pittsburgh Energy Technology Center

A high resolution mass spectrometric (HRMS) screening technique developed at the Pittsburgh Energy Technology Center (PETC) was used to screen process streams from coal gasification and liquefaction for possible hazardous compounds. The screening technique compares precise masses determined by high resolution mass spectrometry to those masses of chemical formulas corresponding to selected hazardous and/or toxic compounds. The hazardous compound list employed in the HRMS screening program is comprised of nearly 700 hazardous compounds from OSHA, EPA, NIOSH, ACGIH, and NAS lists. HRMS screening data was obtained on coal gasification tars and all the major process streams from the PETC 400 lb/day liquefaction PDU. Liquefaction product made with an added catalyst was found to contain fewer possible hazardous compounds than product made without added catalyst as determined by the HRMS screening technique. Concentrations of specific compounds in process waters from both gasification and liquefaction processes were determined by direct injection gas chromatography.

METHODOLOGY DEVELOPMENT FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN FUGITIVE EMISSIONS FROM COAL LIQUEFACTION PROCESSES

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and

Milton L. Lee and Daniel L. Vassilaros

Bringham Young University

The objective of this project is to develop a method for the quantitative collection and analysis of polycyclic aromatic hydrocarbons (PAH) in fugitive emissions from coal liquefaction processes. Coal liquefaction products and

Toward this objective, it has been shown that FAH can be quantitatively recovered from from ambient air, and the collected sample can be quantitatively recovered from the collection media by solvent extraction, using n-pentane. Further, dilute solutions of PAH in n-pentane can be concentrated by solvent removal using a solutions of PAH in n-pentane can be concentrated by solvent removal using a supple losses. The Kuderna-Danish evaporative concentrator, with minimal sample losses. The chromatographic resolution of complex mixtures of PAH expected to be present in fugitive emissions from coal liquefaction processes is best attained using in fugitive emissions from coal liquefaction processes is best attained using high resolution glass capillary—gas chromatography. The gas chromatographic retention characteristics of over 200 PAH have been determined, and a new gas chromatographic retention index system unique for PAH has been developed. The PAH retention index system provides for the tentative identification of numerous PAH in these complex mixtures. Positive identification is obtained when the retention indices are combined with mass spectral data on the same chromatographic peaks. The use of the new PAH retention index system will be demonstrated by the analysis of an aromatic fraction from a coal liquefaction product.

INTEGRATED COMPLIANCE AND CONTROL TECHNOLOGY RESEARCH ACTIVITIES
FOR IN SITU FOSSIL FUEL PROCESSING EXPERIMENTS

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U.S. Department of Energy
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Fossil fuel processing research facilities must comply with Federal and state regulatory standards. In addition, the experimental sites provide research opportunities to evaluate control needs and then design and demonstrate control measures as each technology approaches commercialization. This paper will summarize the regulatory compliance and control technology activities and illustrate their integration as pertaining to field in situ recovery experiments for oil shale.

Battelle Pacific Northwest Laboratories

Wastewater disposal is an important element to be considered in evaluating the environmental impact of the developing shale oil industry. Wastewater can be generated by a number of different sources within a shale oil recovery facility, depending on the type of recovery system used, the location, and the type of oil shale processed. The pollution potential of the wastewater may be very high as in the case of retort water or it may be low as in the case of some minewaters. Above-ground retorts may reuse all wastewater streams generated within the mining and processing facilities to moisten spent shale for compacting in the dumping areas. Moisturizing spent shale is not performed at in situ operations; therefore, substantial wastewater discharges are anticipated at their installations. In situ retorting produces water in approximately the same volume as the oil produced, consequently a 100,000 barrel per day facility would generate about 4 million gallons of retort water each day for disposal.

Studies have been completed on the evaluation of land disposal and underground injection as disposal options for shale oil wastewaters. Land disposal is the application of wastewater at the soil/air interface to utilize natural chemical and physical reactions for purifying the wastewater. Underground injection makes use of deep confined aquifers or isolated geological zones for discharge of wastewaters. The results of this investigation indicate that both the wastewater characteristics and the climate of the oil shale regions of Colorado, Utah, and Wyoming are not favorable for land disposal of retort water. Underground injection is a viable disposal option for retort water where geological conditions are favorable; however, regulatory restraints are expected to limit the use of this option.

Studies are currently in progress on benchscale evaluations of treatment technology for retort water and mine water. Conventional biological treatment appears to be adversely affected by toxicants in the retort 'water, however, preliminary results indicate that the addition of powdered activated carbon may overcome this problem. Several different methods have been investigated for removal of fluoride, boron, and alkalinity from minewaters. Ion exchange is a leading candidate for treatment of minewaters.

Burned out oil shale retorts need to be stabilized to prevent subsidence of the overburden and the ground surface; prevent gas leakage; maximize resource utilization; and provide subsurface disposal of spent shale that has been retorted on the surface and minimize ground water contamination.

We believe that in order to stabilize the retorts, the following strategy should be followed.

- (1) Characterize the components of the retort such as overburden and pillar strength: temperature effect on strength; retort and pillar permeability; and rubble behavior during and after retorting.
- (2) Develop slurry that can accommodate a maximum amount of spent shale and low quality water.
- (3) Investigate techniques for emplacing the grout and sealing the retorts.
- (4) Develop a retort cooling process whereby sensible heat can be recovered and the residual rubble will have properties amenable to grouting.
- (5) Prepare a full scale field test program to evaluate the optimum combination of cooling procedures, grout and emplacement techniques.

U. S. Department of Energy Bartlesville Energy Technology Center

The injection of wastes into deep underground formations is the most economical method for disposal of liquid wastes that are not amenable to surface treatment. Operating costs are lower for pretreatment and subsurface disposal than for surface treatment systems, and plant area requirements are less. Chemical treatment is minimal, and generally the only physical treatment required for underground injection is filtration. This report presents a broad view of modern industrial underground waste injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

The petroleum industry has been injecting fluids into subsurface formations for many years; therefore, many of the techniques and much of the equipment for handling industrial liquid wastes are already available for industrial waste disposal or can be modified to meet the specialized requirements. The techniques for drilling and completing the disposal wells have been perfected, and the equipment to do it is in service. Similarly, the behavior of fluid flow through porous rocks and unconsolidated sand has been investigated; therefore, many of the theories and equations describing the fluid distributions have been proved. Modification may, however, be needed to make them applicable to waste injection systems and to describe the radial chromatographic properties of the injected wastes constituents.

A subsurface disposal system can be successful only if a porous, permeable, formation of wide areal extent is available at sufficient depth to ensure safety in storage and retension of the injected fluids. The wastes usually are treated for solids removal and compatibility with the formation. An impermeable zone, such as shale or evaporite, must overlie the injection horizon to prevent vertical migration of the waste or displaced formation brines into low-salinity aguifers above the disposal zone.

General principles of design and construction are applicable to all subsurface injection systems; therefore, this report is presented in three parts. First the general technology of subsurface disposal systems is presented with notations on cost; second, the general geology of the United States is discussed with reference to subsurface waste disposal; and third, detailed discussions are presented on disposal systems that illustrate particular design and operating features.

Pittsburgh Energy Technology Center

Paper not submitted for publication in Proceedings.

SCREENING COAL GASIFICATION AND LIQUEFACTION PROCESS STREAMS FOR POSSIBLE HAZARDOUS COMPOUNDS

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Paper not submitted for publication in Proceedings.

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ABSTRACT

Fossil fuel processing research facilities must comply with federal and state regulatory standards. This paper summarizes the research effort in effect at the Laramie Energy Technology Center and regulatory requirements pertaining to control technology for process waters associated with in situ oil shale processing. In addition, the experimental sites provide control needs and then design and demonstrate control measures as each technology approaches commercialization.

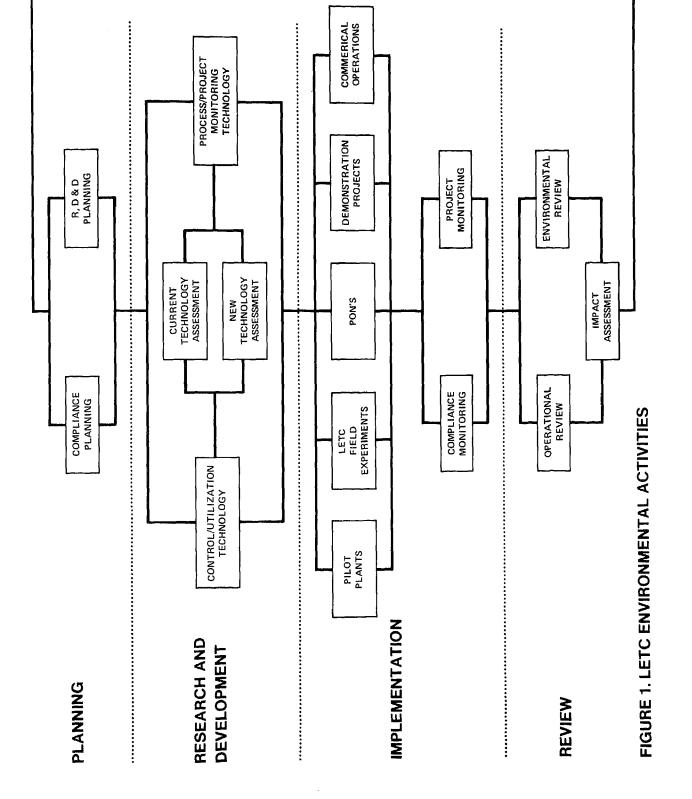
INTRODUCTION

The Laramie Energy Technology Center (LETC) is primarily responsible for the development of in situ recovery technologies related to such alternate fossil fuel resources as oil shale, coal, and tar sands. Advancing in situ technologies to commercial practicability involves a progression of field experiments through which the engineering, environmental, and economic issues can be explored and resolved. In 1977, legislation was passed requiring federal facilities to comply with federal, state, and local regulations and standards when conducting field experiments. Environmental efforts at LETC address compliance requirements at field sites and generate information that can be transferred to industry and environmental regulatory agencies as in situ technologies approach commercialization. This paper will illustrate, through specific examples, the development of control technology in conjunction with compliance requirements.

BACKGROUND

The goals of the environmental effort at LETC are (1) to identify, quantify, assess, and reduce to within acceptable levels any adverse environmental impact that may result from in situ fossil fuel processing field experiments conducted by LETC and (2) to accelerate the acquisition and application of environmental and compliance data related to in situ fossil fuel processing so as to move the technologies towards commercialization.

The development of in situ processing technology is primarily accomplished through a schedule of field experiments. Environmental research



coordinated and integrated use of every field experiment to further both process and environmental RD&D efforts. In many instances, environmental work is conducted outside of the field activity (e.g., laboratory, review, or assessment work). Nevertheless, under the LETC approach such work is either derived from or oriented towards a field activity.

The general approach for the environmental activity at LETC is shown in Figure 1. This diagram illustrates the primary areas (in boxes) associated with various stages of environmental activity as it progresses from planning, through R&D, to implementation, and review. These stages are iterated to account for the changing implementation focus as it progresses from pilot plant facilities to commercial operations. Within this framework, all subjects of environmental concern are addressed, including potential air, water, land, ecologic, socioeconomic, occupational, and aesthetic impacts.

It should be evident from Figure 1 that the scope of environmental work at LETC is quite broad. LETC in house field activities are also numerous. with projects currently in progress near Bonanza, Utah and Rock Springs. Wyoming (oil shale), Hanna, Wyoming (underground coal gasification), and Vernal, Utah (tar sands). To more effectively illustrate the interrelationship of compliance activities related to field projects with other environmental efforts, specific subjects have been selected; namely, the Rock Springs experimental in situ oil shale facility and control technology for in situ oil shale process waters. Water-related problems are pertinent to all in situ technologies from both regulatory and research points of view. this discussion will address a significant subject in some detail, while at the same time it will serve to illustrate the LETC approach of coordinating and integrating process and environmental research at the field level for all technologies. A summary of environmental research conducted by LETC for in situ oil shale processing, which includes reference to process data, has recently been published (1).

DISCUSSION OF CONTROL TECHNOLOGY FOR PROCESS WATERS

In this paper the term "process water" refers to all contaminated waters originating in conjunction with the in situ oil shale process. Process waters are derived from the following primary sources: (a) water formed as a byproduct of the combustion of organic matter in oil shale, (b) water released by dehydration of oil shale minerals, and (c) native groundwater associated with or intruding into the retorting zone (1). As a result of their intimate association with the retorting process, these waters become heavily laden with both organic and inorganic constituents. A summary of water quality parameters for process waters derived from both simulated and true in situ retorts is presented in Table 1 (2). This table indicates that process waters characteristically are alkaline and contain high levels of solids and dissolved organics. Principal inorganic constituents include ammonia, ammonium, bicarbonate, carbonate, magnesium, sodium, and various sulfur species. The organic constituents are primarily polar in nature, with carboxylic acids

Parameter	Range		Average	Best Value ^C
Alkalinity, total (mg/l CaCO ₃)	18,200	110,900		16,200 ± 480
Aluminum	0.041	16.6		<0.03 - 19.1
Arsenic	0.46	10	1.8	1.0 ± 0.2
Barium	0.002	0.47	0.07	0.71 ± 0.33
Beryllium	<0.001	<0.001		<0.006
Bicarbonate, mg/ll HCO3	4,200	73,640		15,940
Biochemical oxygen demand, 5-day	350	5,500		740
Bromine	<0.001	1.94	0.082	2.4 ± .4
Cadmium	<0.001	0.005		0.0016 ± 0.0008
Calcium	0.0	94	7.6	12 ± 4
Carbon, inorganic, mg-C/2	1960	19,200	7,500	3340 ± 390
Carbon, organic, mg-C/2	2,200	19,000	4,700	1003 ± 192
Carbonate, mg-CO ₃ /2	0.0	15,210		500
Chemical oxygen demand	8,500	43,000	18,500	8100 ± 5700
Chlorine	0.007	1910		824 ± 61
Chromium	0.009	0.08	0.015	0.02 ± 4%
Cobalt	0.002	0.65	0.12	0.030 ± 0.012
Conductivity, µmhos/cm	15,100	193,000	31,000	20,400 ± 3840 0.10 ± 0.04
Copper Fluoride	0.003 0.1	160 270	0.019	60 ± 9
Hardness	20	1,500	88	110
Iodine	<0.001	1.3 77	7.6	0.59 ± 0.30 1.2 ± 0.3
fron	0.091 0.002		0.1	0.0045 - 0.02
Lead	<0.002	0.83 7.1	0.70	0.18 - 0.8
Lithium				
Magnesium	3.2	350	22	20 ± 6
Manganese	0.001	0.39	0.099	0.09 ± 0.04
Mercury	<0.001	0.39		0.0003 - 0.021
Molybdenum	0.033	1.2		0.60 ± 0.07 0.06 ± 0.02
Nickel	0.014	2.6		
Nitrogen, ammonia, mg-NH ₃ -N/ℓ	1,700	13,200	7,000	3795 ± 390
Nitrogen, ammonium, mg-NH ₄ -N/l	930	24,450	10,000	3470 ± 830
Nitrogen, nitrate, mg-NO ₃ -N/ℓ	1.4	8.7		0.17
Nitrogen, organic, mg-N/2	73.3	1510		148 · 630 3420 ± 420
Nitrogen, Kjeldahl, mg·N/l	6,600	19,500		
Oil and grease	3,800	3,800	0.7	580
pH	8.1	9.4	8.7	8.65 ± 0.26
Phenois	2.2	169	1,25	60 ± 30 3,2 ± 2.6
Phosphorus Potassium	0.23 8	19.0 120	37	47 ± 9
				0.21 ± 0.11
Selenium	<0,001 <0,001	1.7 0.23		0.003 ± 0.001
Silver	45	1600	320	4333 ± 244
Sodium Solide dissolved	1,750	24,500	6,800	14,210 ± 193
Solids, dissolved Solids, total	6,350	121,000		14,210 ± 120
	2,070	119,300		
Solids, volatile	42	2,200	1,400	1990 ± 250
Sulfur, sulfate, mg-SO [*] ₄ /ℓ Sulfur, sulfide, mg-S [*] /ℓ	0.0	156	.,	0.0
Sulfur, total, mg-S/R	14	2320		2300
Uranium	0.018	93		0.55 ± 0.07
	0.004	~100	0.27	0.12 ± 0.01
Vanadium	0.004	>190 15.1	0.28	0.31 ± 0.04
Zinc	0.020	10.1	V.ZU	2.5 0.07

^a Selected values taken from reference (2). This reference should be referred to for discussions pertinent to each value given above.

^bThe range given is based on the analysis of up to 18 different waters obtained from 4 simulated in situ oil shale retorts. An average value is given only if 15 or more waters were available.

^CBest values determined by a statistical technique in the analysis of results obtained from a multilaboratory, multimethod survey of the Omega-9 sample.

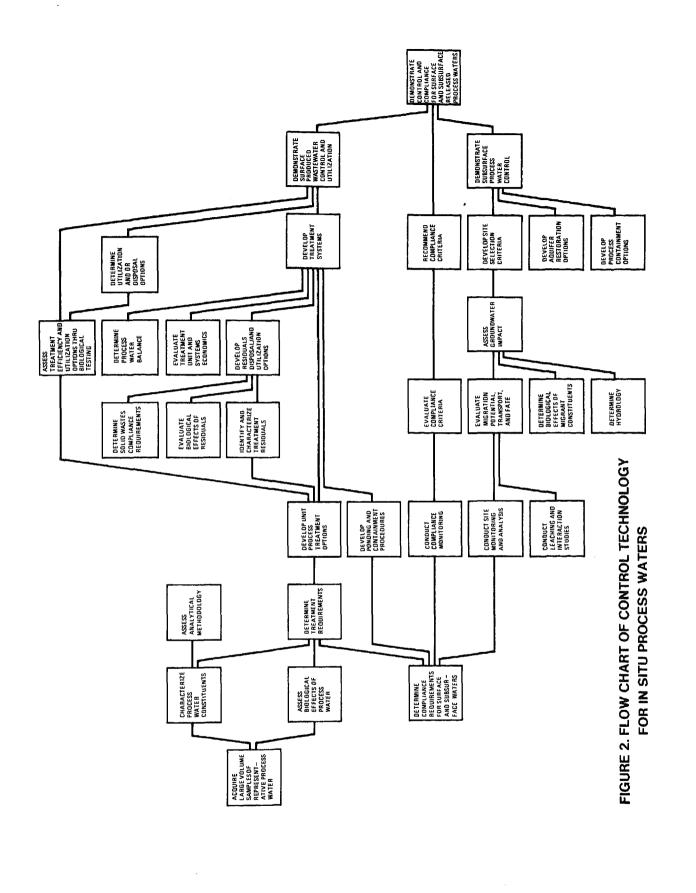
field in situ experiments.

The quantity of process waters produced during in situ oil shale processing is dependent upon several factors, including the mineral content of the oil shale, the volume of groundwater present or seeping into the retorting zone, the duration and areal extent of the burn, the amount of organic resource combusted during retorting, and the amount of injected water (1). The ratio of process water to oil produced at the surface during field experiments has been noted to vary from 0.4 to 22.2 (1). The minimum volume of surface-produced process water derived from in situ processing is estimated to be near the volume of oil produced (1). This minimum volume would amount to nearly 5,000 acre-feet of process water per year for every 100,000 barrels of shale oil produced per day.

The preceding discussion establishes that low quality process waters originating from the in situ process will have both a surface and a subsurface disposition, both of which pose potentials for environmental contact. The intrusion of groundwaters into retorted zones and their subsequent contamination is another source of possible subsurface disturbance. The goal of process water-related control technology research at LETC is to demonstrate, in conjunction with all applicable compliance criteria, techniques for the effective control and, where practical, utilization of both surface- and subsurface-released aqueous effluents so as to mitigate any undesirable environmental effects. The achievement of this goal is prerequisite to the establishment of a full-scale, commercial in situ oil shale processing industry. Figure 2 illustrates the steps required and the approach being followed by LETC to achieve the goal of control technology for in situ process waters. This figure is largely self-explanatory, and the remainder of this section will be devoted to a discussion of some of the concepts illustrated. 1

It should first be noted that two primary efforts are being conducted simultaneously; namely, the control of process waters associated with surface and subsurface release. Although not diagrammatically illustrated in Figure 2, many of the work elements provide data and results common to both pursuits (e.g., site monitoring, process water balance determinations, and possible utilization of surface produced waters for subsurface applications, such as steam injection). The determination of appropriate or necessary control, treatment, or utilization options for water released at either the surface or in the subsurface logically precedes systems engineering design efforts. In this program, such a determination is based on two primary inputs. The first input is obtained from examining current or anticipated compliance requirements related to released process waters. The initiating role that compliance

¹ Reference (1) provides key references to work published up to 1978 in the subject areas indicated. Subsequent citations or additional technical information may be obtained from the authors.



design, there is scope for progressive improvement and refinement of these regulations as our knowledge of process water impacts and mitigation options increases.

The second primary input in determining control requirements and options is based on findings and recommendations from research specifically designed to identify impacts resulting from released process waters. Characterization of the constituents in process waters, assessment of the biological effects of process waters, and determination of the migration potential, transport, and fate of process water constituents through site monitoring and laboratory experiments all represent this type of research.

Considering the ever increasing demands on the limited water resources of the semi-arid oil shale-bearing regions of the West, water produced during in situ processing in itself should be considered as a potentially valuable commodity. The possible use of process waters for both on- and off-site purposes is therefore given considerable attention early in the development of unit and process train treatment systems. At this time the most probable uses for excess process waters are related to steam reinjection, site steam generation, heat exchanger and cooling water, and land applications, such as for irrigation during revegetation and rehabilitation of sites. Economic considerations should include consideration of solute recovery from the process waters during treatment as a means of offsetting treatment costs.

An inevitable consequence of any treatment procedure is that a concentration of residuals will be removed from the influent stream. The development of acceptable options for the disposal and/or use of such residuals is considered to be a fundamental part of the overall development of an acceptable treatment system. The multiplicity of potential uses and the rather unique compositional characteristics of process waters considerably limit the applicability of existing water treatment technologies to process water treatment needs. It is therefore necessary that a variety of treatment methodologies -- spanning primary, secondary, and tertiary treatment by physical, chemical, and biological means -- must be explored simultaneously to determine their capability for handling these type waters. There is currently a broad effort under way in this area (1). In the meantime, field experiments will continue to produce excess effluents. A temporary measure available now is to contain such waters until functioning treatment systems are in place. Also, evaporation ponds established at field sites offer excellent opportunities to study ponding practices.

An assessment of the impact that subsurface released process waters and leachates from retorted zones may have on groundwater quality is an active research objective at field sites. Should groundwater quality changes be determined as profound and persistent, then the obvious mitigation procedure would be to select in situ processing sites where the hydrologic, stratigraphic, or other considerations would be such that groundwater disturbance or degradation would be prevented. However, this recourse would limit the amount of available resource. It is therefore necessary that other options for mitigating groundwater impacts be explored. Methods for the containment

The starting point, and the final proving ground, for process water control technology development is in the field environment. It is here that relevant water samples, containing all the variances imposed by the process, are obtained. It is in this environment that the dynamic factors (migration, bioavailability, ecological effects, utilization options) are at work. Thus, it is at these locations where the control technology must first be demonstrated.

DISCUSSION OF WATER-RELATED COMPLIANCE REQUIREMENTS

Now that some important dimensions of process water control technology have been discussed, it is necessary to examine the legal and regulatory structure within which such processes must function. This section will examine both Federal and Wyoming environmental laws and regulations that impinge upon the implementation of in situ processing technologies involving both surface and subsurface water.

Laws and regulations apply to air pollution, water pollution, land reclamation, toxic substances, solid waste, occupational safety, health, and many other aspects of in situ processing. As noted earlier, we will address environmental regulations as they apply to surface and subsurface water.

Surface Waters

The Federal Water Pollution Control Act (FWPCA) (3) established goals to eliminate discharge of pollutants into navigable waters by 1985 (4); to achieve interim goals of water quality which provides for the protection and propagation of fish, shellfish, and wildlife (5); and to prohibit discharge of toxic pollutants (6). In order to achieve these goals, industrial facilities can be regulated through three different mechanisms -- standards are established for maintenance of the quality of receiving waters; standards of performance can be established for specific classes of emission sources; and standards can be established for specific toxic pollutants.

Standards Based on Quality of Receiving Water

The FWPCA bases effluent limitations on water quality of the receiving water:

Whenever. . . discharges of pollutants from a point source or group of point sources . . . would interfere with the attainment or maintenance of that water quality in a specific portion of the navigable waters which shall assure protection and propagation of a balanced population of shellfish, fish, and wildlife, and allow recreational activities in and on the water, effluent limitations (including alternative effluent control strategies) for such point source or sources shall be established which can reasonably be expected to contribute to the attainment or maintenance of such water quality (7).

Standards of Performance for New Effluent or Emission Sources.

In addition to effluent regulations based upon the quality of receiving waters, the FWPCA orders EPA to establish "National Standards of Performance" for new effluent or emission sources in 27 different industries. "Standards of Performance" are defined as:

...a standard for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator of EPA determines to be achievable through the application of the best available demonstrated control technology, process, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants (8).

In establishing standards of performance, the EPA administrator will take into account the cost of achieving effluent reduction, non-water quality environmental impact, and energy requirements (9).

After standards of performance are promulgated, it will be unlawful for any owner or operator of any new effluent or emission source to operate the new source in violation of any standard of performance applicable to such source (10). Regulations are now in existence for more than 40 different industries. Oil shale, of course, is not specifically regulated at this time.

Standards for Toxic Pollutants.

The FWPCA also mandates that the EPA administrator must maintain a list of toxic pollutants (11). Each toxic pollutant listed is subject to effluent limitations resulting from the application of the best available technology economically achievable for the applicable category or class of point sources (12). Criteria for best available technology economically achievable shall include characteristics of pollutants (chemical, physical, and biological), amounts, and the degree of effluent reduction attainable through the application of the best control measures and practices achievable, including treatment techniques, process and procedure innovations, and operating methods.

Section 307.(7) of the FWPCA also states, "Prior to publishing any regulations (establishing best available technology economically achievable), the EPA should consult with appropriate advisory committees, states, independent experts, and federal departments and agencies." Emerging technologies such as in situ oil shale processing should be prepared to make informed input to EPA.

If discharges meet the criteria established for (a) receiving waters, (b) best available control technology economically achievable for the applicable industry or (c) toxic pollutants, the EPA or state regulatory agency to which the authority has been granted may issue a permit for the discharge of any pollutant. The permit is a National Pollution Discharge Elimination System (NPDES) permit (13).

water quality of the receiving water. While performance standards are subject to research, existing field facilities must comply with regulations designed to protect the quality of the receiving body of water.

Each state was given the opportunity to adopt water quality standards for the water of its state. Wyoming defines its water to include both surface and subsurface waters. The EPA has approved Wyoming's surface water quality standards and allows Wyoming to enforce the National Pollution Discharge Elimination System's permit system. In addition to surface water quality standards, standards for pollution of groundwaters are being proposed in Wyoming.

In Wyoming the law prohibits any person, except when authorized by a permit, to alter the physical, chemical, radiological, biological, or bacteriological properties of any waters (14). The Wyoming act also forbids construction of any facility capable of causing or contributing to pollution. While standards of performance do not exist for the oil shale industry, LETC research facilities must comply with regulations based upon water quality for receiving waters. Hence, extensive data must be obtained for compliance purposes.

Subsurface Waters

Regulation of subsurface water pollution is rapidly developing. Wyoming recently proposed water quality criteria for seven classes of water. Contamination of subsurface water will then fall under their permitting system. Wyoming intends to maintain the physical, chemical, radiological, biological, and bacteriological properties of its subsurface waters. Consequently, in situ industries must be able to prevent contamination or restore water to its original condition.

Regulations promulgated under the Safe Drinking Water Act (15) will require State underground injection control (UIC) programs to prevent underground injection which endangers drinking water sources (16). Critical to the in situ oil shale industry will be definitions of "underground drinking water sources" and "underground injection."

The Act defined underground injection as the subsurface placement of fluids by well injection (17). Proposed definitions (18) defined well injection as "subsurface emplacement through a bored, drilled, or driven well." The proposal also defined an underground drinking water source as "any underground source with a level of total dissolved solids of 10,000 mg/l or less" (19).

The "regulations may not interfere with or impede (a) the underground injection of brine or other fluids which are brought to the surface in connection with oil or natural gas production, or (b) any underground injection for the secondary or tertiary recovery of oil or natural gas, unless such requirements are essential to assure that underground sources of drinking water will not be endangered by such injection" (20).

which have a total dissolved solids level below 10,000 mg/l which will not be protected because they are oil producing, are severely contaminated or located in such a way that use as drinking water is impracticable" (21).

Subsurface water quality standards will be extremely important to in situ oil shale development. The selection of in situ processing sites so that they do not interfere with subsurface waters or the development of restoration methods for such waters to their original quality are important considerations for control technology.

EXAMPLE PROJECTS INTEGRAL TO COMPLIANCE AND CONTROL

The previous discussion points out that there are federal and state regulations on water quality standards for both surface- and subsurface-produced aqueous effluents to which a potential in situ oil shale processing industry must adhere. Also field experiments must comply with all applicable regulations and meet established criteria for water control. In the absence of rigorously defined techniques and systems to control and simultaneously utilize produced waters, field experiments must employ certain expediencies which are acceptable under the law. An example of this is the use of containment and evaporation ponds constructed in accordance with state regulations and guidelines. While limited at this time in terms of employing sophisticated control technology capabilities at field sites, such sites do nevertheless offer prime opportunities for developing and demonstrating such capabilities. Despite of current limitations in applied control technology, field experiments can be conducted so as to meet applicable compliance criteria. The use of an evaporation pond serves to illustrate this point.

An evaporation pond will be used for disposal of process waters during operations at Rock Springs Site 12 (scheduled for operation in November 1978). This pond was designed to contain 100,000 gallons of water, was constructed in accordance with Wyoming Division of Environmental Quality (DEQ) guidelines for wastewater ponds, and required a permit from that agency. With respect to monitoring, the state requires that a leak detection system be incorporated as a design feature of the pond. However, research activities which will be associated with this pond also will include monitoring and analysis of volatile emissions, measuring evaporation characteristics, analysis of surface layer materials, analysis of dissolved solutes and changes resulting from weathering and biological activity determination of the amount and content of residues, and monitoring solar radiation, wind speed, wind direction, and ambient temperature. In addition, studies of pond liner compatability with process waters and shale oil were performed prior to the selection of the liner used in the pond. These studies exceed those required by the state, but utilize the opportunity afforded by the pond to better define pond characteristics. The additional data to be obtained from the Rock Springs Site 12 evaporation pond will provide the first characterization of physical and chemical aspects associated with ponding of process waters. These data

as a sedimentation step), these additional data will augment our knowledge of control procedures and options.

Discussion of the environmental research related to acquiring an in situ mining permit from the Wyoming DEQ for operation of Rock Springs Site 12 will serve as another example of projects integral to both compliance with regulations and development of water control technology. The in situ mining permit requires evidence of specific plans to restore any disturbed aquifer so that the water quality is equal to or better than it was prior to the activity. Figure 2 illustrates that, with respect to subsurface process waters, the ultimate objective is to demonstrate appropriate control so that no adverse environmental impact will occur. Three control approaches for achieving this are shown in the figure -- site selection, aquifer restoration, and process containment. The current plan leading to aquifer restoration will be discussed after a few remarks pertaining to the other two approaches.

The first approach is related to site selection criteria. The development of site selection criteria means that one must determine what type and to what degree subsurface environmental data are required in order to locate an in situ process where no groundwater impacts will occur even if ancillary subsurface control features are not used. It is possible that appropriate site selection would not require additional control of subsurface process waters if it could be established that there would be no contact between these waters and native groundwaters. Detailed hydrologic and geologic data may be required to determine such a finding. Specifically what data is required to allow for such site selection (including compliance data) is the focus of this approach.

The second approach, development of containment options, entails defining ways of lessening any intermingling of subsurface process waters with resident groundwaters. Diversion of aquifers up-dip of retort zones might be one option to be considered in this approach.

In the third approach, aquifer restoration, the present plan involves three interacting areas of activity. These are: site monitoring; solute leaching, transport, and interaction research; and field restoration trials. Each of these three activities will be discussed in turn. Site monitoring activities pertain to pre-operational, operational, and post-operational monitoring and analysis of subsurface waters located within, peripheral to. and at some distance from fracturing and in situ retorting experiments. Significant examples of this activity can be found in conjunction with Rock Springs Sites 4, 6, 9, and the current Site 12 operation (1). Post-operational monitoring of Site 4 has been in progress since this site was retorted in 1969. Monitoring of backflood waters, a subject significant to the leaching of spent retorts, is a part of each of these site activities. The water monitoring program being conducted in conjunction with Site 12 was developed using knowledge gained in prior experiments and will serve as a focal point for overall assessment of subsurface migration phenomena resulting from in situ experiments conducted in the Rock Springs area. In order to facilitate this task, all relevant water quality data are assembled in a computer system

At the same time, several studies are in progress dealing with the physical and chemical interactions associated with subsurface-produced water release and migration. Such studies include examinations of the leaching of retorted shale, the interaction of process waters with consolidated subsurface soils, sediments, and aquifer materials, and solute transformations in waters remaining or migrating from the retort zone. These studies are primarily oriented towards defining the mechanisms underlying phenomena observed during monitoring. This knowledge also will aid in the extrapolation of trends witnessed during monitoring activities to predict the ultimate probable fate and disposition of subsurface waters associated with in situ processing.

The third activity essential to the aquifer restoration plan involves field trials at the Rock Springs area. The previously described activities will serve to quantify and model aquifer disturbances. This field activity will explore and test methods for correcting any such disturbances. A preliminary step is the evaluation and selection of procedures. Two options are currently under consideration. One is to seal the retorted zone to prevent future contact between groundwaters and spent shale, and thus eliminate possible contamination through leaching. A project has been initiated in this regard which will select and test possible sealing agents (grout, cement, polymers, etc.) (22). One limitation of this option is that it does not address the question of process waters which may have been released during the course of retorting. Another option is to recover the process/groundwater eminating from the retort area and to treat such water at the surface to a degree suitable for reinjection into the retort zone. There is currently some evidence to suggest that a few cycles of this type would be sufficient to remove leachable materials from the retorted shale surface (22). This option would appear to be economically more attractive than the first option, especially since it uses treatment facilities which will be in place to treat surface-produced waters and because it may be relatively easy to equal or improve the quality of groundwaters (particularly at Rock Springs) through a treatment scheme.

As soon as sufficient data are available to decide which of the two options discussed is the more attractive, current plans call for testing the techniques at selected field sites. Use of the Rock Springs sites will take maximum advantage of the extensive site-specific data previously gathered during earlier activities (e.g., monitoring, transport and interaction research, and backflood water analysis). The efficacy of the option being tested could be determined largely through the use of existing monitoring wells. Following evaluation of the first field trial, a second, and more exacting, control experiment is planned. The second experiment is to be executed during 1981 at Site 12. An accelerated effort will be needed to achieve these field experiments. The goal is to demonstrate the selected aquifer restoration technique at Site 12 which will serve to advance our capabilities of subsurface process water control and will also serve to fulfill DEQ requirements for Site 12 as stipulated in the in situ mining permit. Such capabilities will then be available for application to other sites.

Figure 2 related to biological effects research. Biological subjects being studied at LETC encompass terrestrial (plants and microorganisms), aquatic, and animal systems (1). The animal studies are primarily concerned with examining the health risks of occupational exposure to process waters that may be accidentally encountered at field sites or in the laboratory. The terrestrial, aquatic, and animal studies were initiated to fulfill two needs. The first need was to determine the impacts, if any, of process waters associated with LETC in situ processing field experiments on the local ecosystems and their components. This need was raised in the Environmental Assessment prepared for LETC field projects (24) in accordance with regulations established under the National Environmental Policy Act (NEPA). Biological impacts likely to occur as a result of failure of a containment or evaporation pond typifies the kinds of concerns raised in the Environmental Assessment.

The second need was to obtain information that would assist in the development of control technology for process waters. The control of process waters, particularly those produced at the surface, is primarily based on the development of treatment systems capable of upgrading the quality of the waters to a level satisfactory for their intended end use. It is therefore necessary to determine possible end uses of water along with the development of treatment systems. As previously mentioned, excess waters produced during in situ processing should be considered as a commodity. A potentially valuable use of excess waters would be for land applications, such as for agricultural irrigation or for revegetation of disturbed sites. application is to be pursued, then it is necessary to determine the level of treatment required in order to produce a water acceptable for land application. Characterization of constituents in treated and untreated waters and evaluation of legal restrictions on the quality of waters intended for surface disposal are two activities which help to determine required treatment levels. Screening the response of potential target organisms to process waters at various stages of treatment is a third activity being conducted at LETC to assist in the definition of treatment requirements. Through such biological screening studies, it is possible to determine what solutes or fractions in process waters are primarily responsible for adverse effects. Once this is determined, the capability of treatment methods to remove these materials can be considered. The final evaluation of the efficacy of the selected treatment procedure can also be tested through biological screening studies. In this manner, the biological screening work at LETC assists in determining treatment requirements and in assessing treatment procedures for waters potentially to be disposed of in land applications. Biological studies pursued for this purpose are deemed to be as integral to the overall development of control technology as the analytical characterization studies.

SUMMARY AND CONCLUSIONS

There are federal and state regulations on surface and subsurface water pollution. Emerging in situ fossil fuel technologies must be cognizant of these and develop process water control measures to insure compliance.

Energy Technology Center to use in house field activities for advancement of process water control technology while insuring compliance with regulations.

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INTRODUCTION

Wastewater can be generated by several different sources within a shale oil recovery facility. The volume and quality of the wastewater from a particular source is dependent on the location and characteristics of the oil shale processed and on the type and size of recovery system used. The pollution potential may be high as in the case of retort water, or low as in the case of irrigation quality groundwater pumped from a mining area. Inclusion of an upgrading facility at a shale oil recovery complex will also impact the volume and quality of wastewater generated. Above-ground retorting facilities may reuse all of the wastewater streams available for moisturizing spent shale, although this is not necessary for all processes. Since moisturizing of subsurface spent shale is not required for in situ operations, wastewater may be discharged at these sites. However, modified in situ operations could use wastewater for moisturizing spent shale if shale mined from the in situ zones is retorted at the surface. In situ operations generate retort water in approximately the same volume as that of the crude oil produced. Therefore, a 50,000 barrel per day in situ facility would generate about 2 million gallons (16,000 m³) of retort water per day. By comparison, an above-ground retort may generate only 200,000 gallons (1,600 m³) of retort water per day at the same level of oil production.

This paper addresses studies undertaken at Pacific Northwest Laboratory to assess current technology for the treatment and disposal of shale oil wastewaters to maintain acceptable water quality levels in the receiving waters of the oil shale regions presently under development. Although the shale oil industry is largely in the pilot plant/demonstration phase, the codevelopment of adequate wastewater control technology is necessary for several reasons: 1) prevent environmental damage as a result of the pilot plant/demonstration operations themselves; 2) control techniques may produce water which can be reused in the production process and this should be taken into account in the design of full-scale facilities; 3) adequacy of control technology should be fully assessed at an early stage to obviate delays and problems in construction and/or operation of fullscale production facilities; and 4) characterization of effluent discharges from pilot plant/demonstration operations will facilitate other environmental and health assessments. The major oil shale deposits in the United States are located in Colorado, Wyoming, and Utah. Therefore, developers of the shale oil industry must be fully cognizant of the importance of conservation of the limited water supplies in this area.

LAND DISPOSAL

Land disposal of wastewater utilizes interactions between plants and the soil surface and matrix to achieve pollutant removal as the wastewater flows to the receiving water. Passage of the Federal Water Pollution Control Act PL 92-500 has focused attention on land disposal of wastewater as an alternative to be considered for complying with zero discharge requirements slated for 1985. Land

TREATMENT ASPECTS

Pollutant Removal Mechanisms

Removal of wastewater constituents is accomplished by physical, chemical, and biological processes with numerous and complex interactions occurring between these processes. The physical process of filtration provides the removal mechanism for suspended particulate matter in the wastewater. Soil and root microorganisms are responsible for biological degradation of numerous wastewater constituents. Both organic and in-organic compounds are broken down and/or utilized for metabolism by these microorganisms. Chemical processes, such as precipitation, ion exchange, oxidation and reduction, may occur to remove many inorganic and some organic substances. Precipitation of heavy metals, for example, is primarily responsible for removal of these constituents in soil, although ion exchange may be a contributing factor.

Land Application Methods

Existing land treatment facilities can be classified according to two different basic design patterns based on differences in liquid loading rates, land area requirements, and the interaction of the wastewater with vegetation and soil. The first method, infiltration, uses soil as purification medium while the second, overland flow, uses the land surface as the purification medium. Infiltration is further divided into two categories, irrigation and infiltration-percolation, which typically involve low and high rates of application, respectively.

Irrigation is the most common method of wastewater application. This is generally accomplished by sprinkler or spray methods. In areas where irrigation water is scarce, the system is managed to provide the maximum return from a crop, whereas in areas of sufficient water supply, criteria allowing maximum hydraulic loading are followed. Revenue realized from a crop is used to defray operating costs so deciding whether the system is to produce crops or treat effluent is important. Controlling soil salts is vital for plant growth to prevent buildup of toxic concentrations. This is accomplished by managing the wastewater salt concentrations and the rates of application.

Care must be taken to avoid overloading the system which prevents further infiltration of the applied wastewater. The soil can become clogged and the formation of shallow ponds can occur resulting in anaerobic conditions. Anaerobic bacteria can create slimes of incompletely degraded organic matter and particulates which are effective soil surface sealants. Other factors that can cause clogging are: 1) compaction from heavy weight; 2) the movement of fine grains of soil down from the upper zones; and 3) the formation of insoluble compounds from reactions between wastewater constituents and soil water and/or minerals.

when investigating the applicability of land treatment and disposal for a particular wastewater. The general criteria for judging the suitability of a wastewater for land disposal are given below:

- 1. The organic material must be biologically degradable at reasonable rates.
- 2. It must not contain materials in concentrations toxic to soil microorganisms. Since some toxic materials may accumulate through adsorption or ion exchange and approach toxic levels after prolonged operation, there must be reasonable assurance that this effect can either be prevented or mitigated.
- 3. It must not contain substances that will adversely affect the quality of the underlying groundwater. In many instances, decisions relative to this aspect of land disposal systems are difficult because of the uncertain nature of available estimating techniques.
- 4. It must not contain substances that cause deleterious changes to the soil structure, especially its infiltration, percolation, and aeration characteristics. An imbalance of sodium ion is a common problem in this regard.

Characteristics relevant to land disposal are presented for a number of different retort waters in Table 1. $^{(1)}$ All of the retort waters, except that from the Utah in situ test site, are from simulated in situ retorts at the Laramie Energy Research Center and the Lawrence Livermore Laboratory.

High salinity commonly found in the retort water would be toxic to most cover crops. Waters having conductivities greater than 2,250 $\mu mhos/cm$ are considered unsuitable for irrigation in most cases. With the possible exception of one sample for which insufficient data are available (University of Southern California No. 1) none of the retort waters in Table 1 would be below 2,250 $\mu mhos/cm$ conductivity following ammonia removal by stripping. Steam stripping tests would be required to establish accurate conductivity values for the ammonia stripped water.

Substances which could affect groundwater quality at a land disposal site receiving retort water are listed below:

- high salinity;
- high nitrogen concentrations which yield nitrate on oxidation; and
- refractory organics which are not oxidized or removed by the soil.

The high salinity found in most retort waters would adversely affect drinking water quality groundwater if sufficient dilution were not available in the aquifer. A limit of 500 mg/l is recommended for drinking water and this value is exceeded by more than 100% for all the retort waters listed in Table 1, even after steam stripping for ammonia removal. Furthermore, evaporation of water during irrigation and leaching of salts from the soil will add to the dissolved solids content of the retort water as it percolates to the groundwater.

TABLE 1. Retort Water Quality Data Pertinent to Land Disposal

		10 Ton	Simulated	In Situ Reto	rt Runs. Li	ERC ⁽²⁾	
Constituents	S-29	S-31	5-32	5-33	S-35	S-36	S-37
Na ⁺ , mg/l	210	1,300	1,200	160	530	960	150
K ⁺ , mg/l	8	70	47	70	23	23	21
Mg ⁺² , mg/l	3.2	280	140	17	130	350	210
Ca ⁺² , mg/1	0.6	9.8	4.9	4.9	27	29	35
MH ₃ -N [includes NH ₄ ⁺], mg/l	14,200	10,500	13,500	8,900	5,100	4,800	
Total Alkalinity, mg/l CaCO2	40,800	34,000	47,000	20,500	17,200	13,900	8,200
Added Ca^{+2} , (a) mg/1	3,900	1,420	440	4,460	400	1,300	
C1 ⁻ , mg/l	5,000	4,200	3,200	7,900	2,300	4,500	1,100
so ₄ ⁻² , mg/1	1,600	1,600	320	2,100	380	1,800	1,400
Total Na ⁺ , K ⁺ , Mg ⁺² , Ca ⁺² , C1 ⁻ , S0 ₄ ⁻² , mg/l	10,700	8,880	5,350	14,700	3,790	9,140	3,736 ^(d)
Total Filterable Residue, 103°C, mg/l			••				
Total Organic Carbon, mg/1	6,060	3,880	2,830	10,660	4,970	9,370	33,350
Biochemical Oxygen Demand, mg/l							
Chemical Oxygen Demand, mg/l							
Conductivity After NH ₃ Stripping (b)	>2,250	>2,250	>2,250	>2,250	>2,250	>2,250	>2,250

	Univer of Sou Califor No. 1	thern	LERC 150 tonne Retort, LBL(4)	Lawrence Livermore(C) 7 Ton Retort	Utan in situ Test Sita(S)
Na ⁺ , mg/1	312		655	164	3,500
κ ⁺ , mg/l	3.5		37 .	28	90
Mg ⁺² , mg/1	48.4	16.4	24	2.3	16
Ca ⁺² , mg/l	14.9	4.6	3.3	1,5	<1
$NH_{3}-N$ (includes NH_{4}^{+}), mg/l	4,790		8,360	25,000	3,060
Total Alkalinity, mg/l CaCO ₂			38,000	80,500	14,500
Added Ca ⁺² , ^(a) mg/1		• ••	••		0
C1 ⁻ , mg/1		1,560	57		
SO ₄ ⁻² , mg/1	59	930	1,100		
Total Na $^{+}$, K $^{+}$, Mg $^{+2}$, Ca $^{+2}$, C1 $^{-}$, S0 $_{a}^{-2}$, mg/1			1,900		
Total Filterable Residue, 103°C, mg/l			4,210		13,500
Total Organic Carbon, mg/l	3,182	19,000	4,980		
Biochemical Oxygen Demand, mg/l	5,500	350	5,330	3,000	3,400
Chemical Oxygen Demand, mg/l	20,000	12,500	8,800	8,660	8,200
Conductivity After NH ₃ Stripping, ^(b) µmhos/cm			>2,250	3,800 ^(d)	>2,250

⁽a) Ca⁺² added as Ca(OH)₂ for ammonia stripping; Ca⁺² mg/l = (mg/l NH₃ - N/14 mg/meq - mg/l Total Alkalinity/50 mg/meq) (20 mg/meq) (b) Conductivity assumed to exceed 2,250 µmhos/cm when total ions exceed 1,200 mg/l. (c) Analysis by Pacific Northwest Laboratory. (d) NaOH added for stripping ammonia; conductivity measured on steam stripped water adjusted to pH 7.

may dictate the land requirement to attain the desired nitrogen loading. The nitrate and organic -N content of retort water has not been determined on a sufficient number of samples to establish an average or range of values.

Steam stripping of ammonia is more effectively accomplished at high pH levels. Stripping efficiency is reduced as neutrality is approached and becomes low for acidic solutions. Additional alkalinity in the form of lime is frequently added to maintain adequate pH levels. The addition of lime in the stripping process substitutes Ca^{+2} ion for ammonia ion which is beneficial from the standpoint of the ratio of Na^+ to Ca^{+2} plus Mg^{+2} . However, if considerable lime is required, the salinity of the steam stripped waste will be high due to the calcium salts present. The alkalinity deficit reported as added Ca^{+2} (lime) for steam stripping is given for most of the retort waters in Table 1. Removal of all the ammonia may not be required since some nitrogen will be required for vegetation growth and oxidation of the organic matter in the retort water. In addition to ammonia, nitrogen can be supplied by organic-nitrogen and nitrate-nitrogen in the retort water.

The generally high ammonia levels in retort water would be expected to cause toxicity problems if not removed prior to disposal of the water to land. Although removal of the ammonia may be relatively costly, part or all of this cost may be recovered by marketing the ammonia. It is likely that steam stripping would be used to remove the ammonia since this process is well adapted to removal of high concentrations of ammonia from wastewater. Steam stripping is the standard industrial process used for removal of ammonia from coking liquors and petroleum refinery sour water. Sufficient alkalinity must be available in the retort water to allow conversion of NH4⁺ ion to volatile NH3 which is stripped by the steam passing counter-currently to the water in the stripping column. Alkalinity and ammonia data on only one retort water, Utah in situ test site, indicate sufficient alkalinity to steam strip the ammonia. Addition of alkalinity would probably be required for the other retort waters. The total alkalinity reported for these waters cannot be considered an accurate guide, however since the end point pH for alkalinity titration may be well below pH 7. Ammonia stripping efficiency has not been adequately defined to date for assessing this aspect of land disposal. Furthermore, a pilot study may be required to accurately establish the optimal nitrogen loading.

It is possible that some of the organic constituents in retort water will be resistant to oxidation and might eventually be leached into the groundwater causing some deterioration in the quality of the groundwater. A low BOD relative to a COD could indicate a large fraction of the organic matter in the retort water is not readily biodegradable. Therefore, it is anticipated that low loading rates will be required to allow sufficient time for oxidation of the organics by the biota in the soil. The generally high organic content would appear to be the limiting factor on application rates of retort water to land rather than hydraulic characteristics. Furthermore, refractory organics which would not degrade even under low loading rates would leach through to groundwater.

which may cause problems.

Substances which cause plugging of the soil commonly include sodium ion (when it is unbalanced with Ca^{+2} and Mg^{+2}) and suspended solids (nonbiodegradable). Suspended solids can plug the pores of the soil through the process of filtration, while sodium ion can cause dispersal of the clay particles in the soil thus sealing the pore structure. Currently, data are insufficient to evaluate the possible effect of suspended solids in retort water on land disposal, but at least part of the suspended matter in retort water is expected to be removed in the pretreatment steps for ammonia stripping to avoid fouling the stripping column. Air pollution from volatile organic constituents in this waste is also a potential problem. Retort water generally has an offensive odor which would not be well received by downwind recipients from the disposal site. Consideration would also have to be given to the possible presence of volatile toxic organics or other organics which would degrade air quality in the region.

Effect of Climate

The long winters characteristic of the oil shale regions of Colorado, Utah, and Wyoming adversely affect the cost of land disposal by irrigation and overland runoff due to the large wastewater storage requirement. Irrigation and overland runoff are not possible during extended periods of freezing temperatures and application rates must be reduced during cool weather. Based on the length of frost free seasons, storage requirements range from 5 to 10 months, however, specific site operations may decrease the storage area needed.

UNDERGROUND INJECTION

Underground or deep well injection is a disposal method which seeks to isolate a liquid waste in a geologic strata to eliminate, as nearly as possible, any environmental impacts resulting from disposal of the waste. Geologic strata selected to receive wastes by this method are generally located at a considerable distance from ground surface to provide additional assurance of confinement and avoid contaminating freshwater aquifers near the surface. Underground injection is normally reserved for wastewaters which are very difficult or expensive to treat for release to surface receiving waters. It is used extensively for the disposal of oil well brine wastes.

UNDERGROUND INJECTION WELLS

A typical well consists of several pipes extending below the surface. The function of each of these pipes is as follows:

<u>Conductor Pipe</u> - This is the first of several concentric pipes that are placed into a disposal well. It extends between 30 and 60 m below the surface and prevents shallow water contamination while the surface hole is being drilled. This pipe is usually driven into place with a pile driver.

<u>Surface Casing</u> - This pipe extends from the surface to approximately 60 m below the base of the freshwater. This casing is cemented in place back to the ground

casing is also cemented back to the surface and inside the surface casing. Its purpose is to seal off the formation above the disposal zone and below the freshwater.

Injection Tubing - This pipe is the conduit through which the effluent travels to the disposal zone. It is always sealed at the well head and usually just above the disposal zone. The annular space between the protecting casing and injection tubing is filled with a noncorrosive fluid. Pressure should be applied to this annulus approximately $35,000~\rm kg/m^2$ higher than the injection pressure. The higher annular pressure will prevent any flow of effluent into the casing tubing annulus.

Disposal Zone Completion

If the well is completed in a sand formation, the gravel packed sand screen completion method should be used. If the well is completed in a limestone formation, open hole or perforated completions are acceptable.

WASTE CHARACTERISTICS

The suitability of waste for underground injection depends on its volume and physical and chemical characteristics, and on the physical and chemical properties of the potential injection zones and their interstitial fluids. Wastewater that is desirable for injection must be: 1) low in volume and high in pollutant concentration; 2) difficult to treat by surface methods; 3) free of any adverse reaction with the formation fluid or the strata; 4) free of suspended solids; 5) biologically inactive; and 6) noncorrosive.

Waste disposal into underground aquifers constitutes the use of limited storage space, and only concentrated, very objectionable, relatively untreatable wastes should be considered for injection. The fluids injected into deep aquifers do not occupy empty pores, but displace the fluids which saturate the storage zone. Consequently, optimal use of the underground storage space will be realized by the use of underground injection only when more satisfactory alternative methods of waste treatment and disposal are not available.

Reaction of the wastewater with the formation water or the strata is important. Resulting problems could include dissolving the formation, generating a gas or precipitate in the formation, and clogging by biological growths. The wastewater should be free of suspended solids and biologically inactive to avoid reservoir clogging. The corrosiveness of the wastewater should be low to prevent tubing and pump corrosion.

Retort water characteristics vary depending on the type of oil shale, retorting process, and retort operating conditions. As shown in Table 1, BOD5 values range from 350 to 5500 mg/l and filterable residue from 150 to 101,000 mg/l. Ultrafiltration may be necessary to remove the suspended solids. Biocide addition may be necessary because high BOD concentrations promote biological activity.

Ammonia concentrations of retort water vary from 2600 to 31,500 mg/l. Toxic level of ammonia for anaerobic fermentation is 1300 mg/l (toxic level may vary considerably due to synergistic or antagonistic effects of other ions). High ammonia concentrations in the retort water should prevent biological activity. When ammonia concentration is reduced, (either by treatment for ammonia recovery or by ion exchange during migration of fluid in the disposal zone) the probability of biological activity is increased. If necessary nutrients (mainly Ca, Mg, and P) are present in the disposal zone, biological activity of the retort water is almost certain. Plugging of the injection zone by bacterial growth and by gas formation (CH4 and CO2) is likely to occur unless very long residence times in the injection zone are permitted for further reaction.

DISPOSAL SITE SELECTION

Great care must be exercised in the selection of an underground disposal site for liquid wastes. The suitability of a specific location of a waste injection well must be evaluated by a detailed geological subsurface investigation. However, regional geological conditions can be used to evaluate general suitability of certain areas.

Certain areas of the continental United States, such as the Rocky Mountains, are generally unsuitable for waste injection wells because igneous or metamorphic rocks lie at or near the ground surface. Such rocks do not have sufficiently high porosity or permeability to warrant their use as a disposal formation. Areas with extensive extrusive volcanic sequences exposed are also not suitable for waste disposal wells. Even though these rocks have porous zones, they usually contain freshwater.

The final appraisal of a disposal well site is usually determined by a two-phase geologic investigation. The first phase includes an evaluation of potential sites on the basis of available data. The second phase consists of a more detailed evaluation of subsurface conditions based on information obtained from drilling a pilot hole or the injection well.

Information sought during the first phase of the investigation and prior to the installation of an injection well includes the extent, thickness, depth, porosity, permeability, temperature, water quality, and piezometric pressure of potential injection zones. The presence of impermeable confining beds, lateral changes in rock properties, the existence of faults or joints, and the occurrence of any mineral resource in the area must also be evaluated. Existing wells in the area which may penetrate the potential injection zones must be located because liquid wastes could escape through these wells if not properly plugged.

The second phase of the investigation is conducted during the drilling and testing of the injection well. Often the actual injection zone is not selected until the well has been drilled and a number of potential zones have been tested and until the chemical quality of water in the potential zones has been evaluated. Pumping tests are used to measure the permeability and water samples are obtained for chemical analysis. Other important rock properties are measured by geophysical logging, drill-stem testing tools, or by laboratory tests on core samples. The results of these geologic investigations are used not only in evaluating the feasibility of subsurface waste disposal, but also to provide basic data for designing the injection well and the optimal rate of injection.

programs to prevent or eliminate groundwater contamination and to improve sanitary conditions of these waters. In 1974, EPA issued "Administrator's Decision Statement No. 5" as agency policy on injection wells and subsurface emplacement of fluids by well injection. This policy was drafted to protect the subsurface from pollution or environmental hazards as a result of improper injection practices and poorly sited injection wells. Under this policy, EPA opposes the emplacement of wastes by injection without strict controls and a clear demonstration that such emplacement will not interfere with present or potential use of the subsurface environment, contaminate groundwater resources, or otherwise damage the environment. EPA can require that all proposals for subsurface injection be critically evaluated to determine that the following guidelines have been met:

- All reasonable alternative measures have been explored and found less satisfactory in terms of environmental protection.
- Adequate preinjection tests have been made for predicting the fate of materials injected.
- There is conclusive technical evidence to demonstrate that such injection will not interfere with present or potential use of water resources nor result in other environmental hazards.
- The injection system has been designed and constructed to provide maximal environmental protection.
- Provisions have been made for monitoring both the injection operation and the resulting effects on the environment.
- Contingency plans that will prevent any environmental degradation have been prepared to cope with all well shut-ins or well failures.
- Provisions will be made for plugging injection wells when abandoned and for monitoring plugs to ensure their adequacy in providing continuous environmental protection. Also under this policy, EPA acknowledges that subsurface injection of wastes is only a temporary means of disposal until new technology that will ensure a higher degree of environmental protection becomes available.

In December of 1974, the National Safe Drinking Water Act was passed by Congress. The purpose of this legislation was to ensure that water supply systems meet minimum national standards for the protection of public health. The Act was designed to achieve uniform safety and quality of drinking water in the nation by identifying contaminants and establishing maximum levels of acceptability. The major provision of the Act that encompasses the underground injection program is the establishment of regulations to protect the underground drinking water sources by the control of subsurface injection.

Various states are to have enforcement responsibility for groundwater protection. If a state underground injection control program is to be approved by EPA, it must:

- allow powrite for underground duties.
- allow permits for underground injection only when the applicant can prove that injection will not endanger drinking water sources;
- provide for inspection, monitoring, record keeping, and reporting to EPA;
 and
- include no requirements that interfere with underground water or brine injection in oil or gas production, or for secondary or tertiary oil recovery, so long as freshwater aquifers are unaffected.

If a state does not have an approved underground injection control program, EPA should assume enforcement responsibilities.

In August 1976, EPA issued the proposed new 40 CFR Part 146 setting forth the regulations governing stage underground injection control (UIC) programs. The intent of this proposed regulation is to:

- establish minimum requirements for effective state programs to protect existing potential underground sources of drinking water from being endangered by the underground injection of fluids;
- provide improved protection of public health by controlling certain potential sources of underground drinking water contamination;
- provide minimal national control;
- allow a state to exercise maximum flexibility to develop programs to meet their needs, noting that differences exist between states, including geological conditions, use and availability of groundwater, and intensity of underground injection operations; and
- provide a program that would not be excessively costly to the states or to most injectors.

TREATMENT OF RETORT WATER

Bench-scale treatability studies are being conducted to evaluate current technology for the removal of pollutants from shale oil wastewaters. Retort waters generated by pilot plant and in situ test facilities are used in these studies to assess the adequacy of treatment processes to achieve the desired effluent quality. The wastewater treatment process selected for evaluation are essentially patterned after technology used by petroleum refineries.

EVALUATION CRITERIA

In the absence of sufficient waste treatment data to develop guidelines for disposal of retort or process wastewater to surface receiving waters, tentative evaluation criteria based on state standards are provided in Table 2. Except for total dissolved solids, these values are taken from water quality standards

1	BOD ₅	30 mg/1
2	Suspended Solids	30 mg/1
3	Oil and Grease	10 mg/l and no Visible
•		Sheen
4	На	6.0-9.0
5	Settleable Solids	Essentially Free From
5 6 7	Floating Solids	Essentially Free From
7	Taste, Odor, Color	Essentially Free From
8	Toxic Materials	Essentially Free From
9	Total Dissolved Solids	500 mg/1

Note: Numbers 1-4 above provide specific limitations for discharge of wastes not covered by other industrial effluent limitation guidelines in the State of Colorado. Numbers 5-8 are standards applicable to receiving waters for Colorado, Utah, and Wyoming. Number 9 is the average total dissolved solids in the Colorado River at Grand Valley, Colorado.

and effluent limitations for the states most likely to be involved in shale oil development (Colorado, Utah, and Wyoming). The limitation of 500 mg/l for total dissolved solids represents an average value for the Colorado River at Grand Valley, Colorado, which is in the vicinity of several planned commercial shale oil recovery operations. Discharges of effluents containing more than 500 mg/l TDS into the Colorado River in this area could ultimately increase the salinity above control limits for this river as it crosses the border into Mexico. Total suspended solids for retort waters listed in Table l exceed 500 mg/l with but one possible exception (USC No. 1) after ammonia removal. Discharge of retort water to surface receiving waters is, therefore, unlikely without desalination.

Four out of five BOD values listed in Table 1 are two orders of magnitude or greater than the effluent limitation of 30 mg/l given in Table 2. It is unlikely that a practical biological treatment scheme could meet this limitation, however, subsequent chemical coagulation, sedimentation, filtration, and activated carbon sorption should achieve a very high level of removal. If this sequence of treatment processes cannot meet the limitations presented in Table 2, less stringent criteria may be applied. In some areas more stringent criteria may be necessary to protect local surface receiving waters.

Retort water can potentially contain several toxic materials. Ammonia, which is highly toxic to fish and other aquatic organisms, is present at relatively high concentrations. Most of the ammonia must be removed before biological treatment can be used to degrade organic material contained in this waste. Arsenic is also present at several mg/l in some retort waters and could interfere with biological treatment. Furthermore, removal would be required prior to discharge to surface waters. Other unidentified substances (e.g., organic substances) could also cause toxicity problems in biological treatment or in surface receiving waters.

BENCH-SCALE TREATABILITY STUDIES

Steam Stripping

Bench-scale studies were conducted to evaluate steam stripping as a means of removing ammonia from retort water. The steam stripper used in this work consisted of a two-inch ID glass pipe packed to a depth of four feet with 1/4-inch ceramic saddles. Feed to the stripper is introduced at the top of the column of saddles and is counter-currently contacted with steam generated by a reboiler at the bottom of the column. Steam, containing volatile constituents stripped from the feed, is removed from the top of the column, condensed, and collected in a condensate receiver. The condensate receiver is vented to a water trap and an acid trap in series to absorb ammonia vapor carried over with non-condensable gases. The steam stripped feed collects in the reboiler and is drawn off continuously to maintain the desired liquid level in the reboiler. Two operational modes were evaluated, one with recycle of the condensate and one without recycle. The condensate is recycled by injecting it into the feed stream to the stripping column. Recycle of the condensate eliminates the necessity of dealing with a separate wastewater stream but also reduces the efficiency of ammonia removal in the stripping column by increasing the ammonia concentration in the feed streams. The alternative of no condensate recycle results is an aqueous ammonia solution which contains volatile organic matter stripped from the retort water.

The steam stripping studies were performed using a sample of retort water from an in situ operation in Utah which contained 3100 mg/l ammonia. Ammonia removal with recycle of the condensate averaged 90% for 2 runs at a boiloff rate of 4.5%. Over 99% of the ammonia was removed without recycle of the condensate at a boiloff rate of 5.3%. Steam stripping also reduced the alkalinity from 14,300 mg/l to about 4,700 mg/l. However, the pH of the retort water increased from 8.8 to about 10 because of carbon dioxide stripping. Excessive foaming occurs in the reboiler which requires precise liquid level control to prevent the foam from entering the column where it causes flooding.

Some fouling of the packing in the stripping column was observed, which may have been the result of suspended matter depositing on the packing. Although settled retort water was used, it contained about 150 mg/l of suspended solids, which were reduced to about 30 mg/l through the stripper. A small volume of light oil was also removed by the steam stripping operation. Organic carbon removal by steam stripping ranges from 15 to 20%.

A sample of retort water from the Lawrence Livermore Laboratory (LLL) was steam stripped while operating in the condensate recycle mode at a condensate temperature of $85.5 \pm 3.5^{\circ}$ C. The ammonia was reduced by 99.5% from 26,500 mg/l to 135 mg/l at a boiloff rate of 15% of the combined feed and condensate recycle. This boiloff rate is equal to 18% of the feed flow alone. Approximately 1/4 of the ammonia was recycled with the condensate stream and 3/4 was evolved from the condensate receiver as a gas. The feed flow to the stripper column with the LLL retort water was restricted to about half that of in situ test site retort water to avoid flooding in the column. This is believed to result from a greater gas flow (CO2 + NH3) up the column with the LLL retort water.

at the Lawrence Livermore Laboratory, one from an above-ground retort in Colorado, and the other three samples from an in situ test site in Utah. Both aerobic and anaerobic biological treatment processes have been evaluated on a bench-scale. Aerobic treatment consisted of activated sludge or combined roughing filter (trickling filter) and activated sludge. The results of the aerobic treatment studies indicated toxicity problems in the treatment units as the concentration of retort water was increased in the feed to the units. Good biological growth and organic carbon removals were observed during the initial phases of the acclimation period but an apparent toxicity problem develops as the percent actual retort water in the feed increases and the percent artificial retort water decreases. Analysis of the retort water for toxicants revealed the presence of arsenic and thiocyanate. Thiocyanate is not believed to be a problem since the concentration of this constituent is below the threshold value of 500 mg/l for activated sludge. Arsenic could be a problem since it exceeds the threshold value of 0.1 mg/l for activated sludge. The Livermore sample contained 1.3 mg/l arsenic and the remaining samples contained 4-13 mg/l arsenic. Results of anaerobic digestion studies conducted with 3.5 liter digesters also indicated toxicant problems. Gas production from the digesters diminished steadily as the concentration of actual retort water was increased.

Results of studies to evaluate powdered activated carbon addition to the anaerobic digesters indicate successful operation in the case of the Livermore retort water, but continued toxicity problems with the other retort water samples. The powdered activated carbon is effective for removing certain soluble organics, including toxic organics, from solution which could reduce the stress on microbial population in the digesters. The activated carbon is also effective in some instances for removing heavy metals from solution, but its effect on arsenic in retort water is unknown at the present time. Analysis for soluble arsenic in the digester receiving in situ test site retort water revealed 0.96 mg/l which is near the toxicity threshold for anaerobic digestion. Soluble arsenic in the digester receiving Livermore retort water was 0.56 mg/l. Preliminary results indicate that activated carbon treatment of Utah in situ retort water will permit aerobic biological degradation to take place although the amount of activated carbon needed may be relatively high.

MINEWATER TREATMENT

Water pumped from underground oil shale mines or in situ operational zones in an oil shale formation may contain pollutants, such as fluoride, boron, and high dissolved salt concentrations, which will prevent unrestricted release of this water to surface receiving streams. Treatment and disposal technology for these minewaters is also being assessed.

FLUORIDE REMOVAL STUDIES

Treatability studies were conducted to evaluate methods for removing fluoride and boron from minewater. The results of bench-scale experiments with groundwater taken from a site in Colorado show a 50% breakthrough capacity of 350 bed volumes for fluoride removal by activated alumina adsorption. The groundwater fluoride concentration was 20 mg/l; therefore, the fluoride capacity is approximately 7 g/l of activated alumina. In order to achieve effective fluoride

to the feed at the beginning of the exhaustion cycle to neutralize the residual caustic regenerant in the bed. The acid addition for pH adjustment of the feed is expected to represent a substantial portion of the chemical cost of treatment for fluoride removal by activated alumina adsorption. An estimated 13¢ per thousand gallons of groundwater would be required to adjust the pH with sulfuric acid priced at \$50 per ton of acid. Regenerant costs are estimated to be 16¢ per thousand gallons of groundwater treated based on sodium hydroxide priced at \$280 per ton.

Results of precipitation experiments with simulated groundwater indicate 90% fluoride removal with phosphoric acid and lime addition. Approximately 9 moles of phosphorus and 10 moles of calcium per mole of fluoride are required to achieve this level of fluoride removal which would be needed to allow discharge of the groundwater to nearby surface receiving waters. The precipitation formed is basically a mixture of fluorapatite, $Ca_5F(PO_4)$, and hydroxy apatite, $Ca_5(OH)(PO_4)_3$. The cost of phosphoric acid and lime to treat the groundwater is estimated to be about \$2 per thousand gallons, which is excessive relative to other treatment methods.

Ion exchange with a weak base anion exchange resin was investigated as a unique process which showed some potential because of the low selectivity of this resin for bicarbonate, the principal ion competing with the fluoride. Laboratory results showed a correspondingly low selectivity for fluoride which negates possible advantages this process may have over other ion exchange processes.

BORON REMOVAL STUDIES

Boron removal from the groundwater is not effected by either activated alumina or lime and phosphate treatment. Bench-scale studies with a boron selective ion exchange resin indicate good boron removal from 2000 bed volumes of groundwater containing 0.6 mg/l. Boron removal to less than 0.3 mg/l is required for discharge to nearby surface waters.

SUMMARY AND CONCLUSIONS

Current data in the literature indicate that the salinity of retort water from shale oil recovery operations will be too high in most cases for irrigation of cover crops needed for effective stabilization by land treatment and disposal. Furthermore, large storage lagoons would be required to hold the retort water during the long winters encountered in the oil shale regions of Colorado, Wyoming, and Utah. Additional problems which may arise with land disposal include air pollution from volatile constituents and groundwater pollution from refractory organics and dissolved salts in the retort water.

Regulatory restraints are expected to limit the use of underground injection for disposal of highly polluted shale oil wastewaters. Proof of confinement of injected wastes will be required to assure protection of drinking water resources, and this is often difficult and costly to accomplish. Underground injection of wastewater is a viable disposal option, however, where all reasonable alternatives have been explored and found to be less satisfactory in terms of environmental protection.

Fluoride removal from minewater with activated alumina and fluorapatite precipitation was investigated. Reagent costs for the precipitation were estimated to be \$2 per thousand gallons whereas reagent costs for activated alumina treatment were only 29¢ per thousand gallons. Boron was effectively removed by ion exchange on a boron specific resin.

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INTRODUCTION

In modified in situ (MIS) oil shale retorting, the resource is processed in the ground. Porosity is introduced into the formation by mining out from 20 to 30% of the in-place oil shale. This material is brought to the surface and either processed in surface retorts or stockpiled. The balance of the material is rubblized underground using various mining techniques. Oil is extracted by pyrolysis and combustion.

This process produces oil, a low BTU gas and process water and leaves behind large underground chambers (retorts) of spent shale and surface piles of raw or spent shale. The acceptability of MIS retorting may depend on the resolution of several environmental issues related to these residuals including groundwater disruption, resource recovery, retort stability and solid and liquid residual disposal.

The purpose of this paper is to investigate the feasibility of returning the solids stockpiled on the surface and process water to the abandoned underground chambers. We believe that potential environmental problems can be largely overcome by returning on-site waste materials to the abandoned underground retort. This would fill the void space created by mining, thus improving structural strength and reducing permeability to groundwater flow. If sufficient strength could be developed, it may be possible to design retorts so that the pillars could be retorted and resource recovery improved. It would also result in the simultaneous disposal of solid and liquid residuals.

CONTROL STRATEGY

Various materials could be introduced into an abandoned retort or surrounding strata to increase structural strength or to reduce the flow of groundwater through the retort. These materials, called grouts, have been widely used in a number of fields including oil field reservoir engineering, nuclear waste containment, gas storage in underground formations, deep coal mining, soil consolidation and various construction activities. The nature of these conventional materials needs to be explored to determine the types of grouts that may be produced from on-site waste materials and properties required for retort sealing.

- tion of local ground water or surface water.
- (2) The grouting material must be chemically stable in the presence of saline groundwater.
- (3) The grout viscosity must be low enough and the setting time long enough for the slurry to penetrate a large area.
- (4) The grouted area should be able to withstand both hydrostatic and overburden pressures. The hydrostatic pressure is due to natural head differences that exist between the aquifers surrounding the oil shale deposits in some areas and to significant dewatering during retorting.

An impressive array of commercially-available grouting materials has been used in other industries. These have been extensively described in the literature (1, 2) and include cement and chemical grouts. Cement grouts typically have long setting times, are non-Newtonian and have relatively high viscosities compared to chemical grouts. Chemical grouts are water solutions of various inorganic or organic compounds and are most typically based on sodium silicate, acrylamide, polyphenolic and urea-formaldehydes, lignins, and resins. Properties and cost factors for some of these grouts are compared with spent shale in Table 1. Preliminary estimates indicate that it could cost from 20 to 270 dollars per barrel of oil for the grouting material alone if abandoned retorts were sealed with these conventional materials. Spent shale grouts, on the other hand, may be economically feasible if technical problems associated with their use are resolved.

The high costs of conventional grouts and the on-site availability of some of the raw materials necessary to manufacture them, suggests that waste products be used to produce grouts. Readily available materials include raw and spent shale, latent heat within the retort, gases, process water and mine water. These materials should be considered as raw materials for on-site manufacture of grouts that would not be economically competitive if purchased from commercial sources. Many of these components show promise for use as grouting materials. Some possibilities include on-site conversion of raw or spent shale into a pozzolan or cement, use of NH $_3$ in the gas and process water to produce urea-formaldehyde polymers, use of CO $_2$ in the gas and Na $_2$ CO $_3$ in the process water to produce insoluble carbonate deposits, and the manufacture of silica gels from mine water, retort waters or offgas.

There are many possible solutions to the retort abandonment problem using these on-site waste products. The most appropriate one will depend on desired strength increase, permeability reduction, retort/aquifer geometry and cost. The following sections of this paper will discuss the use of spent shale and process water as major components of a grout and methods of distributing the grout in the retort.

Comparison between conventional grouting materials and spent shale Table 1.

					Potential Applic	1 Applic
Class	Example	Viscosity before gelling, cp (range)	<pre>Gel time min. (range)</pre>	Cost factor relative to neat cement	Hydraulic	Provid tural
					Darrer	Medium
Cement	Portland cement slurry (neat)	(a)	10-300	1.0	×	×
Silicate	Water glass (sodium silicate)	1.5-2	0.1-60	1.3	×	×
	Injectrol G (3)					
Polymer	AM-9 polyacrilamde (1)	1.2-1.6	0.1-300	7.0	×	×
	PWG (3)	1.5	->300	0.6	×	×
Resins	Herculox (3)	13	7-60	4.5	×	×
	Epseal (3)	80–90				
Emulsions	Asphalt 65% (4)				×	
Foams	Polyurethane foam (5)		1.5	1.5	×	
Spent shale	Lurgi (6)	(a)	28 days	0.05		
Lignin base	Blox-All (2)	8-15	3-90	1.65	×	
Unsaturated fatty acid	Polythixon FRD (2)	10–80	25-360		×	
Elemental sulfur		7 cp @ 159 C	sets when cool	available at low cost from gas refining sites		
Formaldehyde base	Urea-formaldehyde (2)	3.5–13	1-60	0.9	×	

Depends on the water-cement ratio (WCR) and presence of additives. With a WCR of 45%, and no additives, the viscosity cement is 200 cp. Addition of a slurry fluidizer (i.e., naphthalene polymer) may reduce this to 20 cp. By comparison of 450% to 900% is needed to reduce the viscosity of Lurgi spent shale to 200 cp. (a)

compared with pozzolans in Table 2. This comparison shows that spent shale appears to meet the chemical requirements for ASTM Class C pozzolan and is very similar to natural pozzolans. This is of considerable interest because the spent shale could be used to reduce permeability and provide strength development of an abandoned MIS retort.

Two studies have been conducted on the use of surface spent shale to manufacture a cement-like material. However, these have met with limited success (possibly due to low temperatures reached in the surface retorts). Culbertson, Nevens and Hollingshead (7) studied the stabilization of spent shale from a TOSCO retort. Shear strength and confined compressive strength in the range of 250 to 500 psi were obtained. Strength development was positively correlated with the amount of cohesive hydrates formed. After 15 days of setting, no loss of strength occured in samples resaturated with water.

Nevens, Habenicht and Culbertson (6) studied the filling of a simulated in-situ retort with a slurry of Lurgi spent shale. Samples calcined at 750 to 850 C required from 500 to 1000 wt % water to reduce the viscosity to 100 cp. Compressive strengths obtained after 28 days ranged from 5 to 200 psi.

Although results with 100% spent shale grouts have been discouraging to date, research is in its infancy and advances may occur. The most promising possibility is to use spent shale to create a hydraulic lime-pozzolan mortar. This is a mixture containing active lime (CaO) and pozzolanically active silica (SiO₂) and alumina (Al₂O₃) which yield cohesive hydrates when mixed with water. This strategy is explored here by contrasting the chemistry of cements, pozzolans and mineralogical changes that occur during oil shale retorting.

Cement, pozzolan and oil shale chemistry

The chemistry of pozzolan and cement and of the carbonate/silicate minerals in oil shale is germane to understanding the potential role of spent shale as a grout. Cements are prepared by blending proper proportions of finely ground limestone and clay and firing the mixture in a kiln at 1450 to 1550 C. The resulting clinker is cooled, about 5% to 6% gypsum is added as a set retarder and the mixture is pulverized. When water is added to this material and the paste is allowed to set it will gradually convert to a hardened product. This process can be represented by the following set of chemical equations:

Calcining

Limestone or
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
 (1)

$$Clay \xrightarrow{\Delta} Al_2o_3 + Sio_2 + Fe_2o_3$$
 (2)

Table 2. Composition of pozzolans and spent shale

		Oxide analysis, weight percent	ight percent	
Constituent	typical natural pozzolan (9)	typical industrial pozzolan (lignite fly ash) (10)	combustion run spent shale	ASTM C-618-78 class C pozzolan (11)
Si0 ₂	55.0	28.7	46.5	
$^{A1}_{2}^{0}_{3}$	17.7	12.0	10.7) >50.0
Fe_2O_3	3.5	6.8	4.2	1
CaO	3.2	40.5	17.2	1
MgO	1.0	7.4	7.8	ı
so ₃	ı	2.5	ı	<5.0
FeO	6.0	ı	ı	ı
K_2^0	6.4	1	3.0	ı
$^{\mathrm{Na}_2}$ 0	3.4	9.0	3.3	I
Loss on ignition	6.3	0.4	1.6	0.9>

$$2CaO + SiO_2 \xrightarrow{\Delta} 2CaO \cdot SiO_2$$
 (4)

$$3CaO + Al_2O_3 \xrightarrow{\Delta} 3CaO \cdot Al_2O_3 \tag{5}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \xrightarrow{\Delta} 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$$
 (6)

Hydration

$$2(3CaO \cdot SiO_2) + 6H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$
 (7)

$$2(2CaO \cdot SiO_2) + 4H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$
 (8)

$$3Ca \cdot Al_2O_3 + 16H_2O + CaSO_4 \cdot 2H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 18H_2O$$
 (9)

$$3CaO \cdot Al_2O_3 + 26H_2O + 3CaSO_4 \cdot 2H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$
 (10)

It would not be economically feasible to manufacture cement on site because of the high energy requirements (8). However, a hydraulic lime-pozzolan could be produced at temperatures much below clinkering temperatures.

Pozzolans are siliceous and aluminous materials that react with lime in finely divided form and in the presence of moisture to form cohesive hydrates. These hydrates are the main strength-giving compounds of hydrated cement. Typical pozzolanic reactions are:

$$2SiO_2 + 3Ca(OH)_2 \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$$
 (11)

$$A1_2O_3 + 4Ca(OH)_2 + 1OH_2O \longrightarrow 3CaO \cdot A1_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$$
 (12)

These equations show that if active silica and alumina react with lime, calcium silicate and calcium aluminate hydrates are formed. These compounds are similar to those that give strength to portland cement. The ability of a siliceous or aluminous material to react at normal temperature as shown is called "pozzolanic activity" and is measured by ASTM Method No. C 311-77 (11). A sufficient degree of pozzolanic activity may be present in spent shale or it may be increased by heat treatment, or by modifying retorting conditions, or by lime addition.

If pozzolanic activity could be induced in surface spent shale by modifying retort operating conditions, it may be possible to manufacture a hydraulic lime-pozzolan on site. This is more attractive than formation of a cement since activation of silica and alumina takes place at lower temperatures than the formation of clinker compounds (900 - 1000 C). For maximum development of cementitious properties, additional lime may be required. This could be added before retorting or afterward. Fine grinding of the spent shale would be required. Because the clinker compounds of portland cement, formed in equations (3) through (6), would not be present, the grout would set more slowly and have a lower final strength.

on the partial pressure of CO₂. Above 1000 C the calcium oxide reacts with silica to produce calcium silicate compounds (3CaO·SiO₂, 2CaO·SiO₂) and other nonreactive compounds (gehlenites and akermanites). These reactions are summarized as (12):

$$Ca(Mg_x, Fe_{1-x})(CO_3)_2 \xrightarrow{\Delta} (1-x)FeO + xMgO + CaCO_3 + CO_2$$
 (13)

$$2FeO + CO_2 \xrightarrow{\Delta} Fe_2O_3 + CO$$
 (14)

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \tag{15}$$

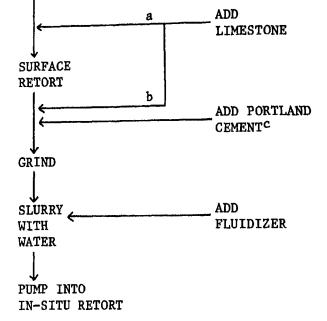
$$nCaO + mSiO_2 \xrightarrow{\Delta} Ca_n Si_m O_{(n+2m)}$$
 (16)

The temperature at which these reactions occur is very important in considering the use of oil shale as a cementitious material. Most surface retorts operate at less than 600 C, which is too low to form a mixture of active silica and active alumina with cementitious properties. Therefore, if spent shale is to be produced for use as a grouting material, the surface retorting process may have to be optimized for pozzolan formation as well as for oil yield.

Based on the foregoing, we propose that the surface retort be operated to produce a hydraulic lime-pozzolan mixture. This recommended strategy is summarized in Figure 1. This figure shows pozzolan production and additives that are being explored in an experimental program. The surface retort is operated to produce a hydraulic lime-pozzolan. The effect of additions of limestone, portland cement and slurry fluidizer are being investigated. The limestone addition would enhance the availability of lime to form cohesive hydrates. If strength of the lime-pozzolan mixture is inadequate, a small addition of portland cement may be desirable. The portland cement would contribute tricalcium (3CaO·SiO2) and dicalcium (2CaO·SiO2) silicate, which, upon hydration, yield Ca(OH)2 and cohesive hydrates. The spent shale pozzolan would react with the Ca(OH)2 as it is formed to yield additional cohesive hydrates as shown in equations (11) and (12). The slurry fluidizer would decrease the viscosity of the slurry so that it could be more easily distributed in the abandoned retort.

GROUT DISTRIBUTION

Grout distribution in abandoned retorts will depend on several factors including grout properties, retort properties and emplacement geometry. Most commercial grouting is performed by point injection from small diameter pipes placed in a grid pattern on centers less than 20 feet apart. This would not be economically feasible due to the large number of deep holes that would have to be drilled. Well spacing greater than or equal to 70 feet



- Add limestone before retorting if retorting temperature is high enough to calcine limestone.
- Add calcined limestone after retorting if retorting temperature is not high enough to calcine limestone.
- C Portland cement addition only if strength development without it is inadequate.

would be needed to make grouting attractive as a method of spent shale disposal if drilling were done from the surface. The effects of the geometry of the grout emplacement, the retort permeability and grout viscosity on retort groutability need to be studied.

Viscosity is the most important grout property for distribution. Spent shale slurries investigated to date have typically had viscosities of 500 to over 1000 cp at low water contents (100% by weight water added) (6). These slurries have generally had viscosity reduction to 50 cp at 200% by weight water added but some slurries have required 1000% by weight water to obtain viscosities less than 100 cp (for comparison, the viscosity of water is 1 cp at 20 C). The relative penetrability of spent shale grout will be strongly dependent on obtaining a low viscosity product (< 50 cp) at low water content (100% by weight water) to achieve desired strength development and permeability reduction.

Permeability of the spent in-situ retort will be the most important property for grout distribution. Uniform penetration of a particulate grout (e.g. spent shale-based grout) may be difficult to achieve because of the heterogeneous nature of the void space of an abandoned in-situ retort. It includes large voids between rubble fragments (up to one inch and more), fine voids where oil shale has been fractured but fragments have not moved apart, fissures and cracks in retort walls, and minutes pores created in spent shale by pyrolysis of kerogen. Invasion of only the larger pores may not be adequate to reduce permeability.

Effective grouting may require complete and uniform penetration of most voids. This will be controlled by the relative size of particles in the grout and the void space in the rubble. In order to penetrate a retort at a reasonable pressure and flow rate, the size of the largest suspended particle should not be greater than about one-third of the size of the voids. Typically, particulate grouts are used for openings that are 1/16 inch or larger and chemical grouts are used for openings that are less than 1/16 inch. Therefore, two injections may be required to seal an abandoned in-situ retort. The first would use a grout with a relatively large particle size and the second would use a nonparticulate grout.

Point source grout injection may not be very effective for grout distribution in abandoned retorts. The grout penetration from a point source is severely limited by the high headloss developed near the tip of the pipe. For most commercial grouts however, set up time is short and point sources are used because not enough grout penetration occurs prior to set up for the well point headloss to become a problem. However, for abandoned retorts, this configuration is not suitable as a large number of injection ports would be required. The cost for this may be excessive. Therefore, line source placement should be explored.

Line source injection is beneficial for increased rubble penetration and faster grout distribution but it is limited by the size of the pipe available to deliver the grout and head required to push the grout through the rubble. A 36 inch pipe diameter flowing at 2 ft/sec could deliver 14 cfs of grout to the rubble. If this grout were delivered to a slotted section approximately 50 feet in length, approximately 8 hours would be

This paper considered the production of a hydraulic lime-pozzolan mixture from spent shale produced in surface oil shale retorts. This mixture could be slurried with process effluents and pumped into abandoned MIS retorts. This control strategy would simultaneously provide for long-term retort stability, minimal groundwater disruption, enhancement of resource recovery and disposal of process residuals. Work completed to date and some theoretical considerations suggest that surface retorts can be operated to produce a spent shale with pozzolanic properties. Additions of limestone. portland cement and slurry fluidizer may be required. Additional work is required to determine optimum retort operating conditions and required additives, and to resolve a number of technical problems. Preliminary cost estimates indicate that this would be an economically viable strategy if technical issues could be resolved. These include high grout viscosities. high water-solid ratios, poor strength development and grout distribution within an abandoned retort. If spent shale grout or some other low-cost on-site waste material cannot be reclaimed for retort filling and plugging. it is possible that MIS retorting may not be both environmentally and economically viable due to the high costs associated with other control strategies. However, if the constraint of enhanced resource recovery is relaxed and if it can be demonstrated that creep and subsidence are not long-term problems, then other lower-cost control strategies may be considered. These would address only the groundwater disruption issues and would include leaching, mine design modifications, grout curtains, and chemical immobilization of leachables.

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ABSTRACT

The injection of wastes into deep underground formations is the most economical method for disposal of liquid wastes that are not amenable to surface treatment. Operating costs are lower for pretreatments and subsurface disposal than for surface treatment systems, and plant area requirements are fewer. Chemical treatment is minimal, and generally the only physical treatment required for underground injection is filtration. This report presents a broad view of modern industrial underground waste injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

The petroleum industry has been injecting fluids into subsurface formations for many years; therefore, many of the techniques and much of the equipment for handling industrial liquid wastes are already available for industrial waste disposal. The techniques for drilling and completing the disposal wells have been perfected, and the necessary equipment is available. Similarly, the behavior of fluid flow through porous rocks and unconsolidated sand has been investigated. Therefore, many of the theories and equations describing the fluid distributions have been proved. Modification may, however, be needed to make them applicable to waste injection systems and to describe the chromatographic properties of the injected wastes constituents.

A subsurface disposal system can be successful only if a porous, permeable formation of wide areal extent is available at sufficient depth to ensure safety in storage and retention of the injected fluids. The wastes usually are treated for solids removal and compatibility with the formation. An impermeable zone, such as shale or evaporite, must overlie the injection horizon to prevent vertical migration of the waste or displaced formation brines into low-salinity aquifers above the disposal zone.

underground waste-injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

Almost any specific waste-disposal problem can be resolved with modern industrial technology, but the processes for waste treatment and disposal are limited by practical economics. The injection of liquid wastes into deep geologic formations is becoming increasingly important. This method is being used especially in the major oil-producing states, where the technology of fluid extraction from, and injection into, underground formations was developed and has been in use for about 50 years.

The experience of the petroleum and chemical industries has shown that underground injection is applicable to all types of liquid wastes, (e.g. mineral and organic acids, bases, inorganic salts, oxygenated and chlorinated hydrocarbons, and mixtures of many other types of compounds).

Subsurface formations have extremely large adsorptive surfaces and contain a diverse population of anaerobic bacteria; both of these factors are beneficial in containing and decomposing the injected wastes. In addition, salts contained in subsurface brines and the diverse chemical constituents of host rocks serve as buffering agents and chemical reactants to aid in the conversion and decomposition of the waste compounds.

If deleterious waste compounds are, indeed, irreversibly adsorbed and decomposed to harmless compounds, the environmental impact of underground waste storage is significantly less than that of chemical waste disposal by burning or discharging to surface streams or the ocean. However, present limitations of knowledge of the possible reaction of waste constituents with subsurface formations impose a potential for creation of an environmental hazard.

TYPES OF WASTES

The selection of subsurface waste disposal as a means of disposing of wastes is based on: (1) the difficulty of treating the waste to an acceptable level of purity for reuse or for discharge to surface streams and (2) the economic margin, if any, between subsurface waste disposal and surface treatment methods.

Some wastes are corrosive acidic or brine solutions of inorganic constituents; some are basic wastes that readily form insoluble hydroxides and other precipitates when mixed with other

designed to process a specific waste mixture for injection into a particular geologic formation.

In this report, the types of wastes being injected into underground formations are classed in three distinct categories: produced oilfield brines, inorganic industrial wastes, and organic industrial wastes, as shown in Tables 1, 2, and 3, respectively. Each of the three types of wastes is subdivided on the basis of the individual waste constituents or of some outstanding property such as pH.

Oilfield Brines

In some oil fields being produced by waterflood, the brine produced with the oil is reinjected into the oil-producing formation for displacement of crude oil. Thus, the brine that would otherwise be a waste product is used for additional oil recovery and economic gain. Additional quantities of water required for a waterflood project are usually obtained from brine wells completed in formations above or below the oil zone.

However, just as many oil fields are being produced by other mechanisms that do not require the injection of brine into the oil-producing formation. In these fields the produced brine is a waste product which is disposed of by injection into subsurface formations from which no fluids are withdrawn. Thus, this operation is similar to the injection of liquid wastes by the chemical industry.

Oilfield brines have a wide range of concentrations of a large variety of cations and anions. Concentrations range from less than 100 ppm to more than 100,000 ppm, as shown in Table 1, where the brines are classified according to the cation and anion in greatest concentration. Most of the produced brines have sodium or calcium chlorides as their major constituents, but magnesium, bicarbonate, and sulfate ions predominate in some. Other ions are present as minor constituents, and in some brines, ions such as bromine and iodine are present in commercially economic quantities (5).

Concentrations of ions from waters of different geologic formations, and in places even at different sites within the same formation, differ widely. Consequently, there are no typical oilfield brines, and generalizations of the chemical reactivity of different brines cannot be made. However, some problems

TABLE 1. - Analyses of Natural Groundwaters Showing Major Constituents of Various Types of Brines (ppm)

Type of Brine	Formation Location	Location	Na	Са	Mg	CJ	нсоз
Sodium chloride Sodium carbonate Sodium sulfate Calcium chloride Calcium sulfate Magnesium chloride Magnesium carbonate Magnesium carbonate	Big Injun Ellis Coalinga Arbuckle Embar Madison Lodgepole Uinta	Pa. Mont. Calif. Kans. Wyo. Wyo. Manitoba 4 Colo.	52,200 3,140 3,290 4,230 140 580 44,900	1,730 390 16,900 140 870 3,260 1,000	3,910 8,80 8,430 30 180 67,340 542	121,000 2,890 2,890 2,520 60,100 1,070 94,900 94,900	70 4,040 360 42 210 1,080 2,140 1,185

closed system, atmospheric oxidation of brine constituents causes the precipitation of salts and hydroxides. Complete removal by filtration is too costly; therefore, aeration equipment is used to complete the oxidation, which is followed by sedimentation and filtration.

Closed systems are used to keep the brine in essentially the same condition that existed in the formation. The closed system is more economical to operate and requires less surface equipment than the open system because the need for aeration and sedimentation is eliminated. Brine is removed from the oil-water separator, filtered, and pumped directly into water wells. Closed systems generally are used where brine is to be injected into a formation other than the oil-producing formation, as a waste-disposal method.

- 2. Scale deposition: Crystals from the concentrated salt solutions tend to accumulate in pipelines and at the face of the formation. They restrict the flow of brine and increase pumping costs. Such scale deposits are controlled by the addition of chemicals, principally phosphates, to the brine at the injection-pump manifold.
- 3. Corrosion: Brines containing dissolved oxygen are very corrosive to ferrous metals. The phosphates added to prevent scale deposition act also as mild corrosion inhibitors, and usually no other corrosion-inhibiting chemicals are added to the brines. However, the corrosiveness of some brines, such as those containing carbonates, may be so great that corrosion inhibitors must be added to prevent loss of surface pipes.

Inorganic Industrial Wastes

Analyses of the inorganic wastes of 18 companies are listed in Table 2 to illustrate the wide variety of chemical-process waste mixtures and to show the stark differences between these wastes and oilfield brines. These wastes have been classified as essentially neutral, basic, or acidic. The neutral wastes, which are low in dissolved organic compounds, are more similar in chemical behavior to oilfield brines than are the others.

The only preinjection treatment required for many of these neutral salt solutions is filtration. However, wastes containing dissolved organic compounds usually complicate underground injection by forming polymeric gums at the formation face and in pores near the well bore.

TABLE 2.--Inorganic wastes that are being injected into deep geologic formations

No.	Description of waste	Injec- tion rate, gpm	Injec- tion pres- sure, psi	Depth of Well, ft	Description of formation
; .	Neutral Wastes NH4Cl (15,000 ppm); NaCl (1,600 ppm); CaSO4 (260 ppm); Na2CrO4 (40 ppm); ZnCl2(5 ppm); urea (4,000 ppm)	006	200	006	Limestone - vugular
2.	(NH4)2SO4 (32%); NaCl (1.5%); nitriles (0.07%) 1 BOD = 10,000 ppm; pH = 6.7	1,000	200	7,000	Sandstone, 700° thick, Ø = 28%; k = 300 md
e,	Na ₂ SO ₄ (800 ppm); NaCl (300 ppm); NaF (20 ppm); NaNO ₃ (3 ppm); FeCl ₃ (2 ppm); MnSO ₄ (2 ppm) ZnCl ₂ (5 ppm); phenols (500 ppm); detergents (300 ppm); pH 7.9, BOD = 50 ppm	20	0	3,000	Limestone - vugular
4	Na ₂ SO ₄ (2,000 ppm); Na ₃ PO ₄ (10 ppm); FeCI ₃ (800 ppm) NaNO ₃ (100 ppm); Na ₂ CrO ₄ (10 ppm); pH = 7.5	80	0	3,800	Dolomite – vugular
5.	NaCl (1,800 ppm); CaCO ₃ (400 ppm); MgCO ₃ (400 ppm) (NH4) ₂ SO ₄ (1,500 ppm); hydrocarbons (1,500 ppm); pH = 8.0	20	007	1,100	Unconsolidated sand; \emptyset = 32%; k = 2,000 md .
٠,	Basic Wastes NaOH (3.0%); Na ₂ SO ₄ (1.0%); Phenol (1.0%); acetone (0.2%); pH = 12	100	300	6,500	Sandstone with beds of sand, gravel and clay. $k = 200-1,000$ md, $\emptyset = 28-32\%$.
7.	NaOH (7.5%); Na ₂ S (1.2%); Na ₂ CO ₃ (2.2%); Na ₂ SO ₄ (0.7%); NaCl (0.3%); PhenolS (0.5%); mercaptans (0.4%); pH = 9.4; BOD = 5,000 ppm	350	400	6,950	Unconsolidated sand, 250' thick
8	NaOH (1.5%); Na ₂ CO ₃ (5.4%); NaCl (13.1%); Glycerine (5.0%); Epichlorohydrin (4.6%); Epoxy resin (1.9%); Phenol (3.2%); acetone (1.6%); ph = 11.2	150	200	6,200	Sandstone with beds of sand, gravel and clay. $k=200-1,000~md,~\emptyset=28-32\%.$

TABLE 2.--Inorganic wastes that are being injected into deep geologic formations (cont.)

on of waste	Injection tion rate,	Injection pressure,	Depth of Well, ft	Description of formation	Years in Opera- tion
95 ppm); NaCl (9,100 ppm); CaSO4, ppm); Mg SO4 (1,500 ppm); NH3 ppm); adipic acid (1,500 ppm); organics (1,000 ppm); pH = 8.5. 1 (6.0%) and HNO3 (4.0%) are added injection pump manifold.	1,100	1,000	5,800	Limestone, vugular, with sand inclusion in some areas. \emptyset = 18%, k = 5 md.	6
0%); NaF (2.8%)	50	150	4,300	Unconsolidated sand	2
000 ppm); NaC1 (32,000 ppm); hydrocarbons- ated (1,500 ppm); pH = 10; COD = 3,000	200	100	7,200	Unconsolidated sands containing shale and clay; \emptyset = 27; k = 1,000 md	ω
<pre>astes .0%); Na₂SO₄ (3,000 ppm); CaSO₄ (800 ppm);)₃ (700 ppm); CrSO₄ (150 ppm) acetic acid m); pH = 1.0</pre>	100	300	3,800	Unconsolidated sand alternating with shale, 1,500' thick, \emptyset = 20%, k = 1,200 md.	N
%); FeCl ₂ (1.8%); FeCl ₃ (1.5%); pH = 2	100	50	4,200	Unconsolidated sand, containing clay and shale, k = 1,500 md, \emptyset = 32%	, ,
$_4$ (0.2%); $_{2}^{80}$ (0.2%); $_{1}^{80}$ (50 ppm) acids (50 ppm); Nitriles (100 ppm),	350	100	4,500	Unconsolidated sand, 800' thick, \emptyset = 32; k = 1,500 md	12
3%); Na ₂ SO ₄ (27.7%); H ₂ SO ₄ (7.8%); HCl H ₂ O ₂ (2.7%); Organic acids (4.7%); Org. les (3.3%); alcohols (1.9%); ketones (1.1%)	30	750	3,700	Sandstone containing chalk. $k = 10-1,000 \text{ md}, \emptyset = 20-25\%$	ω
.%); FeCl ₂ (23.4%)	150	0	2,300	Sandstone, $\emptyset = 12\%$, $k = 100 \text{ md}$	6
8.5%); FeSO ₄ (13.0%)	150	0	2,300	Sandstone, $\emptyset = 12\%$, $k = 100 \text{ md}$	6
0%); $\rm H_2SO_4$ (2.0%); NaCl (10%); acetic (.0%); chloroacetic acid (1.0%); hate hydrocarbons (0.5%)	200	o	4,000	Limestone, vugular	12

TABLE 3.--Organic wastes that are being injected into deep geologic formations

In jec-

Injec-

		tion 1	tion pres-	Depth of	
No.	Description of waste	gbm	psi	Well, ft	Description of formation
, i	Aldehydes Chlorinated aldehydes (1.9%); acetic acid (1.3%); acetaldehyde (0.3%); pH = 5	200	200	5,400	Unconsolidated sands ranging in thickness ft, separated by thin shale beds; $\emptyset=30$
2.	Formaldehyde (0.4%); acetaldehyde (0.4%); Butyonaldehyde (0.3%); crotonaldehyde (0.2%); methyl alcohol (0.2%); butyl alcohol (0.14%); acrolein (0.02%); formic acid (0.01%); acetic acid (0.01%)	850	009	4,500	Unconsolidated sand; Ø = 30-40%; k = 1.0-:
ě	Acetaldehyde (750 ppm); propanol (100 ppm); acetone (350 ppm); acrolein (100 ppm); butanol (150 ppm); methyl ethyl ketone (300 ppm); vinyl methanol ketone (600 ppm); cyclobutanone (600 ppm); dioxane (100 ppm); NaCl (5,000 ppm); NaHCO3 (1,000 ppm); pH = 7.3	800	0	4,000	Sandstone and detrital granite; \emptyset = 25%; 1
4	Alcohols Hexanol (0.10%); amyl alcohol (0.06%); methanol (0.02%); dibasic acids (0.82%); hexamethylene imine (0.14%); cyclohexane (0.02%); dodecane (0.01%); NaNO3 (1.3%); NaHCO3 (0.35%); unidentified organics (2.40%); pH - 9.1	250	450	3,300	Loosely consolidated sand, 260 ft thick. $k=1.0$ - 2.0 Darcy.
5.	Polyvinyl alcohol (300 ppm); methanol (1,400 ppm); acetic acid (400 ppm); hydroquinone (100); silicones (23 ppm); vinyl acetate, (1,200 ppm); methyl acetate (800 ppm); acetalehyde (500 ppm); ehyl acetate (50 ppm); sodium acetate (2,300 ppm); pH = 5	250	200	7,000	Sandstone interbedded with shale.

TABLE 3. -- Organic wastes that are being injected into deep geologic formations (cont.)

No.	Description of Waste	Injec- tion rate, gpm	Injec- tion pres- sure, psi	Depth of Well, ft	Description of formation
.9	<u>Glycols</u> Ethylene glycol (1.0%); K2CO ₃ (1.0%)	350	350	5,000	Unconsolidated
	Ethylene glycol (500 ppm); propylene dichloride (125 ppm); propylene glycol (11,000 ppm); acetone (40 ppm); ethylene dichloride (1,200 ppm); dichloroisoproyl ether (90 ppm); dichloroethyl ether (40 ppm); NaCl (5%); Na ₂ SO ₄ (0.05%); Na ₂ CO ₃ (0.01%)	300	300	000*9	Unconsolidated sand.
8	<pre>Phenols (6.2%); cyanides (1.2%); ammonia (0.3%); thiocyanides(0.1%); NaCl (0.3%)</pre>	100	0	1,800	Sandstone, $k = 200 \text{ md.}$ $\emptyset = 15\%$
•	Acetic acid (0.5%); chloroacetic acid (0.4%); acetaldehyde (0.1%); acetaldol (0.1%); Butanol (0.05%; crotonaldehyde (0.05%); NaCl (0.5%); pH = 2.5, COD = 29, 400 ppm; BOD = 9,900 ppm.	350	400	3,500	Unconsolidated sand. $\emptyset = 27-35\%$; k = 0
10.	Adipic acid (8%); caprolactam (1%); butanol (0.5%); benzene (0.2%); cyclohexane (0.3%); NaCl (2%)	100	350	000*9	Sandstone, $k = 0.2-1.0$ Darcy, $\emptyset = 28\%$
11.	Organic acids (dibasic - principally adipic) (2.6%); nitric acid (0.8%)	400	200	5,200	Loosely consolidated sand.
12.	Acetic acid (3,000 ppm); paratoluic acid (100 ppm); benzoic acid (50 ppm); xylene (100 ppm); methyl ethyl ketone (50 ppm); caCl ₂ (200 ppm); MgSO ₄ (200 ppm); pH = 3.0	200	400	000*9	Sandstone, Ø = 30%; k = 500 md

TABLE 3. -- Organic wastes that are being injected into deep geologic formations (cont.)

		T ă	Depth of	Describitor of formation
<u>ş</u>	Description of Waste	Kpm md8	METTY	מבשרי דל דומו מד שמבחשר דומו
13.	C ₂ -C ₆ organic acids (6,700 ppm); C ₁ -C ₄ alcohols (2,000 ppm); C ₁ -C ₃ kerones (1,400 ppm); propylene glycols (400 ppm); propyl esters (2,000 ppm); propylene oxide (3,000 ppm); C ₅ -C ₆ hydrocarbon (2,000 ppm); Na ₂ SO ₄ (2,000 ppm); NaC1 (500 ppm)	400 800	7,000	Sandstone; Ø.= 27%; k = 300 md.
14.	Acetic acid (160 ppm); maleic acid (100 ppm); xylene sulfonk acid (50 ppm); benzoic acid (50 ppm); butyl alcohol (950 ppm); styrene (100 ppm); isoproponal (100 ppm); phthalic acid (300 ppm); methyl ethyl ketone (250 ppm); NaOH (650 ppm); H ₂ SO ₄ (500 ppm); Na ₂ CO ₃ (350 ppm)	250 1,200	7,200	Sandstone containing beds of clay; k = 200
15.	Nitriles Glycol nitrile (0.5%); iminodiacetonitrile (0.3%); nitrilotriacetonitrile (0.2%); other organic nitriles (1.0%); methanol (0.1%); methyl formate (0.1%); formaldehyde (0.3%); formic acid (0.5%); H ₂ SO ₄ (1.7%); (NH ₄) ₂ SO ₄ (4.3%)	150 200	9,500	Sandstone, 400 ft thick, Ø = 28%; k = 200 o
16.	Disulfides Ethyl disulfide (30%); propyl disulfide (40%); butyl disulfide (25%); mercaptans (5%); water insoluble oil	2	2,200	Unconsolidated sand with thin clay beds, l
17.	Ethyl disulfide (4%); propyl disulfide (6%); butyl disulfide (14%); pencyl disulfide (14%); hexyl disulfide (3%); NaOH (8%)	10 60	1,500	Vugular limestone

disposal of oilfield brines. Pore spaces hear the well bore can quickly become plugged. Insoluble salts of metals in the waste can be deposited in the pores, or hydroxides of metals may form gels that effectively plug the pores. Resinlike materials, such as the epoxy resin in Waste 8 (Table 2), may polymerize in the formation and plug the pores.

Waste mixtures may also react with clay minerals such as montmorillonite and illite (14), found in most sedimentary rocks, causing the clay to swell and reducing the permeability of the formation. This problem is especially troublesome with dilute neutral wastes. Reactions of components in the waste with formation brine or constituents of the formation matrix may cause the evolution of gas, which can produce high pressures and loss of permeability near the well bore.

Where the degree of incompatibility between the formation brine and waste is high, a large volume (200,000 to 500,000 gal) of a nonreactive fluid can be injected ahead of the waste to act as a buffer between the two incompatible fluids. The degree of mixing in the formation between the injected fluid and native brine is relatively small. Mixing occurs in a thin transient zone, and its rate, quantity, and adverse effects depend on the chemical and physical properties of the native brine, the formation, and the wastes. It is only when this mixing occurs in or near the well bore that severe problems arise. The nonreactive buffering fluid injected in front of the waste moves the mixing zone in the formation far away from the well bore so that incompatibility is no longer an adverse factor.

Because inorganic acidic wastes are highly corrosive, they present additional problems of acceptability for underground injection. Corrosion of surface equipment and well components can cause plugging of the formation from the insoluble reaction products. If corrosion can be minimized and initial incompatibility problems eliminated by developing a buffer zone of non-reactive fluid, the injection of low-pH wastes proceeds with ease, regardless of the type of formation selected for injection.

As injection proceeds, the permeability of the formation gradually increases. This fact was demonstrated with rock core samples in the laboratory experiments of Champlin and co-workers $(\underline{4})$. They injected a simulated acidic waste into several outcrop cores and examined the physical properties of the sandstone cores before and after injection of the acidic solutions. In every

loosely bound with cementing materials, and (3) degradation of particles such as clay.

The success that the steel companies are having with the injection of waste pickle liquor (2) into the Mount Simon Sandstone is a good practical example of the injection of highly corrosive acidic wastes. Wastes 16 and 17 of Table 2 are two types of waste pickle-liquor hydrochloric and sulfuric acid, respectively. They contain a high load of iron that amounts to as much as 20 tons/day when injected at the current average rates. The wells disposing of these acidic wastes have been in operation for more than 15 years.

Acidic wastes are also being successfully injected into limestone and dolomite formations (6,7,8). Reactions of these acids with the carbonate formations have not caused adverse permeability problems, perhaps because the carbon dioxide formed by the reaction is sufficiently soluble in the waste and formation brines to be removed from the vicinity of the well bore by the fluid entering the formation.

Organic Industrial Wastes

The analyses of 15 waste mixtures that are aqueous solutions of organic waste constituents, many of which contain dissolved inorganic salts, are divided in Table 3 into categories that are most descriptive of the mixtures. The disulfide wastes (16 and 17 of Table 3) are water-insoluble oils that are being injected successfully without any attempt to make them water soluble.

The aldehydes, phenols, and nitriles have in common a marked tendency to form water-insoluble gums at the face of the disposal formation. Wells injecting such wastes must be stimulated periodically. Acidizing with a mixture of hydrochloric and hydrofluoric acids is the most common treatment, but it commonly is necessary to remove well tubing and reenter the well with drilling tools to remove the accumulation of gum from the formation face. Hydraulic fracturing, induced by pumping liquid in at high pressure until the strata are ruptured, is also employed for stimulation of wells completed in consolidated sandstone or carbonate rock.

The only other troublesome wastes listed in Table 3 are those containing low-boiling-point components that are irritants to the skin and mucous membranes, or are toxic. Wastes 2 and 3 contain acrolein, and Waste 9 contains chloroacetic acid; both

SURFACE EQUIPMENT

Aqueous fluids scheduled for injection into subsurface strata must be free of suspended solids, oil, and gas. The solids create a restriction to flow at the face of the formation, commonly called the "skin effect," and the oil and gas decrease the permeability to the aqueous phase by competing for the flow channels. Therefore, the objective of preinjection treatment of wastes is to remove solids, oil, and gas, or to stabilize a waste that may have a tendency to form a second phase during injection.

The selection of surface equipment depends on the physical and chemical properties of the waste and on the reservoir characteristics of the formation that has been selected for storage. The least complex systems are those designed to process wastes that are noncorrosive and free of suspended solids. The surface equipment required to process this waste includes: (1) a collecting tank; (2) transfer pipes; (3) an injection pump, if surface pressure is required for injection at the maximum flow rate of the waste; and (4) controls, such as float valves and recorders. There are a few such simple installations, but they are not typical because most industrial wastes cannot be injected into subsurface formations without previous treatment at the surface.

Waste from a chemical plant is generally a mixture of several waste streams from separate manufacturing units, cooling-tower blowdown, laboratory sinks, etc. Hence, the waste-disposal system begins with a sewer line that delivers the waste composite to a collecting reservoir of sump. The simplest sump is a cement sump placed several feet below the surface to allow gravity drainage. If the sump has a retention time of less than l hour, sedimentation of suspended solids will not occur to a large degree, and only an occasional raking of the sediment will be required. If a longer retention time is required in the sump, an automatic raking device usually must be installed to prevent sludge accumulation.

Waste-collecting ponds up to 2 million gallons in capacity and lined with an impermeable material may be used. Such large ponds are used to provide a long retention time and also to allow for mixing of the wastes by convection. Hence, these ponds are used where the wastes comprise several waste streams of different composition. A great disadvantage to large ponds with long retention times is the growth of bacteria and algae.

be removed by coagulation and sedimentation. Some wastes contain too much suspended solids for economical filtration, and the solids will not settle in sedimentation tanks without the aid of coagulants. Coagulants are also used where the disposal formation has very small pores, because the pores will be plugged by fine suspended solids that cannot be removed efficiently by filtration.

The size and type of injection pump to be installed are governed by the wellhead pressure, the volume of fluid, and the necessary rate of injection at peak loads. A few installations do not require an injection pump because the hydrostatic pressure of the column of waste in the disposal well exerts sufficient pressure at the subsurface face of the formation to inject the waste. If the wellhead pressure for waste injection is less than 150 psi, simple single-stage centrifugal pumps can be used; but, at higher pressure, multiplex piston-type or multistage centrifugal pumps are needed. Hence, selection of an injection pump must be delayed until the disposal well is ready for operation, and pumping tests can be made.

Some requirements for surface equipment and pretreatment of waste can be determined by testing the waste and the water of the disposal formation. Results of such tests will indicate the compatibility of the formation water and waste, and are useful in determining the treatment required. Even though compatibility can be determined in the laboratory, conditions as they exist underground are difficult to duplicate. A laboratory mixture of the two fluids that apparently is satisfactory may be incompatible in the subsurface, or the opposite may be true. Bernard (3) made some studies by pumping water solutions into sandstone samples that contained incompatible interstitial solutions. He did not observe a decrease in permeability that would have indicated plugging.

Because of the diverse nature of chemical wastes and disposal formations, the surface equipment for a waste-injection system cannot be designed until the formation to be used has been examined. The wastes from chemical manufacturing operations also vary greatly in chemical and physical properties. Therefore, each injection system is unique because the surface equipment is designed to process a specific waste for injection into a specific local portion of a formation. The best way to discuss surface equipment is to cite several examples, ranging from the simplest to the most complex. Three examples selected from the lists of wastes in Tables 2 and 3 are used to illustrate the variety in design and operation of surface equipment.

containing hydrochloric acid as a major constituent. However, the waste mixture is not complicated with suspended solids or undissolved oils that would have to be removed before injection. In addition, initial injectivity tests showed that the geologic conditions permitted the waste to be injected into the disposal formation, a vugular limestone at a depth of 4,000 ft (1,220 m), at the maximum anticipated flow rate under gravity flow. No injection pump was needed to force the waste into the formation, and the absence of suspended solids eliminated the need for filtration. Only a collecting sump and a metering valve to control the flow of waste into the well were required.

A 6-in., steel-jacketed, polyethlylene pipe transports the waste from the control valve to the wellhead, and the fluid pressure in this pipe is monitored. A light oil is maintained under pressure in the annulus of the well to support the fibercast tubing and to detect tubing leaks. A break in the tubing will cause an immediate change of pressure in the annulus.

The flow rate (averaged over a 30-day period) is 200 gpm with a slight vacuum at the wellhead and 35 psi pressure in the annulus. The average temperature of the waste at the wellhead is 120° F. Flow rates fluctuate from 450 gpm, which is in excess of the capacity of the well during periods of heavy rainfall, to a minimum of 110 gpm.

Closed System

A more complex system designed to process Waste 9 of Table 3 is illustrated in Figure 2. The waste is a water solution, very low in pH, containing hydrochloric acid, acetic acid, chloroacetal-dehydes, and chloroacetic acids. Although the organic concentration of the waste generally does not exceed 3% the low-boiling chlorinated hydrocarbon compounds make this a very reactive solution which is extremely irritating to mucous membranes and to skin. Therefore, this waste is handled in a completely closed system.

The selection of materials for construction of the surface equipment was a critical design consideration, because the waste is extremely corrosive to standard construction materials. Epoxy plastic pipe, Hastelloy C, 316 stainless steel, and titanium are used as required.

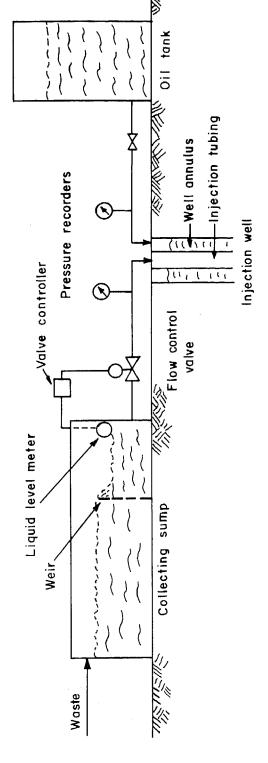


FIGURE I.-Open Surface Equipment Used in One of the Simplest Waste-Injection Systems.

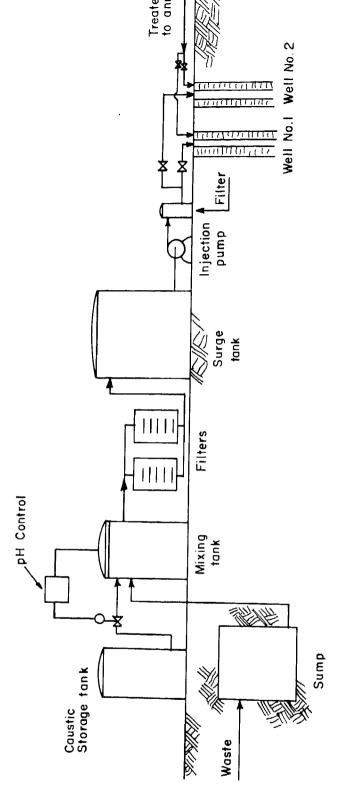


FIGURE 2.— Closed Surface Equipment Used for Wastes Containing Volatile Organic Components.

polymers that precipitate upon standing, and, at a pH greater than 5.0, a tarlike polymer is formed by aldol condensation of the aldehydes.

Following pH control, the waste is filtered in rack-type pressure filters that are designed for backwash and precoat operation as completely closed systems. The processed waste is stored in a surge tank equipped with a liquid-level meter that controls the operation of the injection pump. As a final precaution, just prior to injection into one of the two wells, the waste is passed through a cartridge filter to remove any suspended solids that may have accumulated or formed during retention in the surge tank.

Two wells are maintained because the plant operation is completely dependent on the continued injection of the waste. There are no other provisions for disposal of this waste; hence, if only one injection well were used, failure of the well to receive the waste because of injection-tubing breakage, plugging, or other problems would result in complete shutdown of the chemical plant and considerable economic loss.

The annulus between the injection casing and the tubing is filled with boiler feed water which is reduced in pressure from 800 to 300 psi. The pressure of this fluid in the annulus is monitored continuously as a means of detecting tubing or packer leaks. Two single-stage centrifugal pumps connected in series are used to inject the waste at an average 350-gpm flow rate and 400 psi wellhead pressure.

Complex Open System

One of the most complex of the industrial waste-disposal systems is illustrated in Figure 3. It was designed to process Waste 9 of Table 2 for injection into a "tight" limestone. The waste contains a large load of suspended solids and some oil as it enters the collecting pond. The oil is skimmed from the surface with an automatic skimmer that travels slowly across the pond. The skimmed oil is burned in an incinerator. The waste then is treated with coagulators to accelerate sedimentation of the suspended solids, and with waste hydrochloric acid for pH control.

The sludge from the coagulator and backwash from the filters are sent to a drying bed, and the underdrain is returned to the collecting pond. A series of four leaf filters is used to filter the effluent from the coagulator, and the waste then is stored in

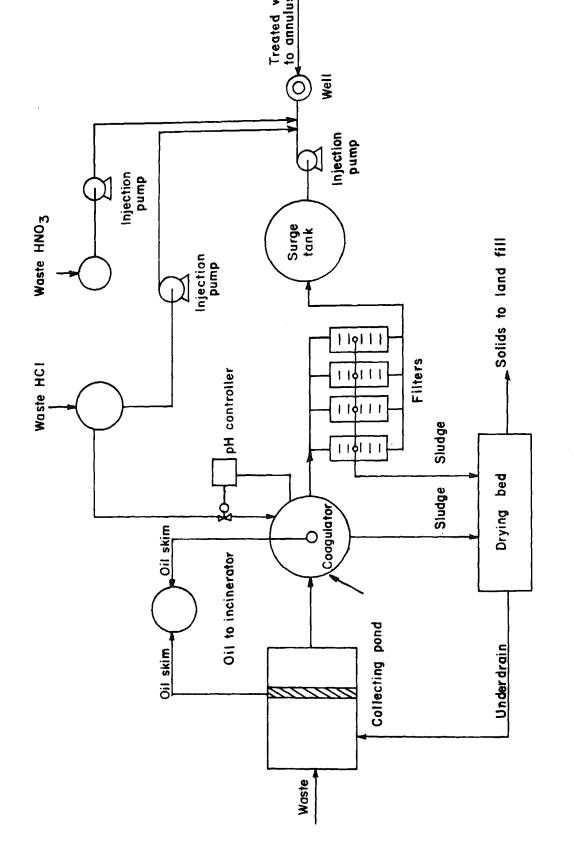


FIGURE 3.-Complex Open Waste Injection System.

injection-pump manifold. The waste acids are collected separately because the waste streams are not constant; therefore, if the acids were added directly to the collecting pond, they would cause wide variations in the pH of the composite waste.

WASTE-INJECTION WELL DESIGN

Drilling and Casing

One of the most important criteria of a waste-disposal well is that it must be designed for complete protection of the near-surface, low-salinity aquifers through which the well is drilled. To accomplish such protection, a 12- to 18-in.-diameter hole is drilled to a depth at least 200 ft (60 m) below the deepest freshwater aquifer encountered. Surface casing (Fig. 4), at least 2 in. smaller than the hole diameter and equipped with centralizers, is run to the bottom of the hole. The annular space between the casing and the well bore is filled with cement. Experience with brine-injection wells has shown that this procedure will protect the freshwater aquifers from contamination if the injection casing is damaged.

After the surface casing has been installed, drilling is continued with an 8- to 12-in.-diameter bit through the potential disposal formations. Core samples of the potential disposal zones should be taken for laboratory examination, and the hole should be logged.

When a suitable disposal formation is selected, a 6- to 9-in.-OD string of casing - the injection casing - is centered in the hole, and cement is circulated to the surface in the annulus between the casing and the well bore (Fig. 4). The well is completed in the disposal zone by one of many methods, depending on the nature of the formation and the waste intended for disposal. Three of the most commonly used completion methods are illustrated in Figure 5.

Well Completion

If the formation is friable, indicating that the well bore may tend to cave and fill the bottom of the hole, a cased-hole completion technique (Fig. 5A) is used to provide positive support for the well-bore walls. For this type of completion, the hole is drilled to the bottom of the disposal formation, casing is set, and cement is circulated to the surface. The

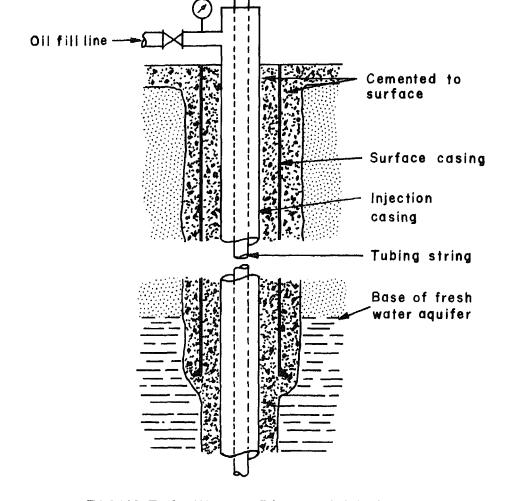


FIGURE 4.-Waste-Disposal Well.

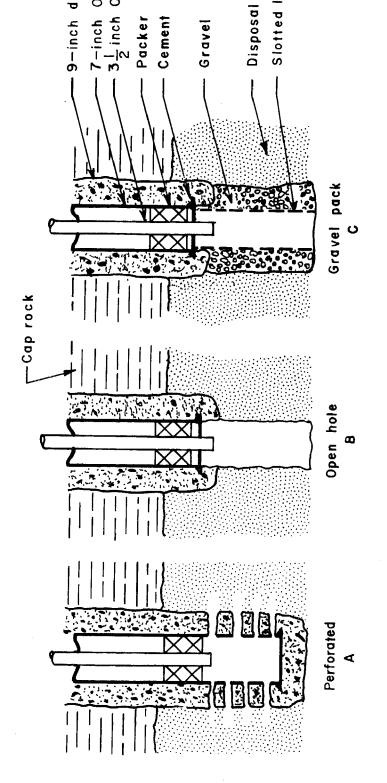


FIGURE 5.- Disposal-Well Completion Methods.

as stainless steel.

Where the disposal zone is a hard consolidated sandstone or a vugular carbonate formation, open-hole completion (Fig. 5B) may be used. Casing is set at the top of the disposal formation and cemented to the surface. Then an open hole is drilled to the bottom of the disposal zone. Open-hole completion also is used if corrosive wastes are to be injected, because products from corrosion of the casing in the disposal zone may plug the formation. Corrosion will also cause casing adjacent to the disposal zone to fail, allowing the cement to crumble and fill the hole with debris.

The third general type of completion, gravel pack (Fig. 5C), is used in unconsolidated sands to prevent sand from filling the bottom section of the injection casing or tubing, and thereby restricting the flow of the waste solution. The sand and gravel pack together at the bottom of the casing to form a tortuous path for the sand moving toward the well casing. The formation sand jams and movement stops; however, space for unrestricted liquid flow is left between the grains of sand and gravel.

Several other completion methods are used in unconsolidated sand. If the well is less than 2,000 ft (600 m) deep, air-lift valves may be installed in the annulus between the casing and tubing. Whenever sand restricts the flow of waste, the bottom section of casing can be cleaned of sand by blowing air through the tubing to lift the sand through the annulus. Another method is to perforate the casing with 1/10-in.—diameter pinholes adjacent to the sand formation ($\underline{10}$). The sand may also be consolidated by treatment with epoxy plastic ($\underline{11}$).

Sometimes the waste is injected directly through the injection casing, but this practice is inadvisable for corrosive waste, even with plastic-coated pipe, since absence of pinholes in the plastic coating cannot be guaranteed. The injection casing is best protected by use of an injection-tubing string inside the casing. Although some tubing strings made of corrosion-resistant metal alloys are used, the most popular material is a fiberglass-epoxy tubing, because of its high resistance to corrosive materials and its light weight.

Usually a packer is installed at the bottom of the long string of tubing in the annulus between the casing and tubing (Fig. 5). Additional protection of the injection casing is

tubing.

A special type of completion is used in some of the wells designed for injection of waste steel-pickling liquor (Wastes 16 and 17, Table 2). A packer is not used at the bottom of the tubing to seal the annular space between the tubing and casing, as illustrated in Figure 5B; instead, electrodes are installed at the bottom of the tubing in the annular space. Water is pumped continuously into the annulus at a pressure slightly greater than the pressure of the waste in the tubing, allowing a constant flow of water through the annular space. The conductivity of water at the bottom of the tubing is monitored to detect accidental entry of acid into the annular space.

This brief discussion of well construction and completion is included only to show the principal features of design. A more complete presentation of the details of construction and procedures used in the construction of waste-disposal wells was given by Baker $(\underline{1})$.

FORMATION CHARACTERISTICS

A subsurface-disposal system can be successful only if a porous, permeable formation of wide areal extent is available at sufficient depth to insure safety for storage and retention of the injected fluids. The stratum must be below all freshwater aquifers and confined vertically by rocks that, for practical purposes, are impermeable to waste liquids. In addition to the protection of usable water resources, the vertical confinement of liquid wastes also protects any developed or undeveloped hydrocarbon and mineral deposits.

Rocks that comprise the earth's crust are classified as igneous, metamorphic, and sedimentary. Of these, sedimentary rocks, particularly those that were deposited in a marine environment, are most likely to have good injection characteristics. Under favorable circumstances, however, both igneous and metamorphic rocks can have sufficient porosity and permeability to receive large volumes of liquid.

Some of the more suitable sedimentary rocks are sandstone, limestone, and dolomite. These rocks usually are porous and permeable enough to be used as injection zones. Naturally fractured limestones, dolomites, and shales may provide satisfactory injection horizons. However, the kind of rock most favorable for industrial waste disposal depends upon the chemical nature of the specific waste to be injected and should be determined for each disposal project.

adequate containment and monitoring of injected fluids.

The injection zone must be isolated, both above and below, to prevent the vertical escape of injected waste. Unfractured shale, clay, slate, anhydrite, gypsum, marl, and bentonite have been found by the petroleum industry to provide good seals against the upward flow of oil and gas (13). The formation thickness required to confine liquid industrial waste cannot be rigidly established. A confining stratum only 10 or 20 ft thick may provide a satisfactory seal to retain oil and gas. However, the risk would be too great to use beds of this thickness to confine industrial wastes because the formation would be very susceptible to fracturing during waste injection and also could contain thin natural fractures as shown in Figure 6.

Sedimentary rocks originally were deposited in uniform layers at the bottom of ancient seas; however, some were later uplifted, folded, and faulted by forces in the earth's crust into anticlinal (positive) and synclinal (negative) structures as shown by Figure 7. Oil and gas often occur in anticlinal folds because they are less dense than water and seek a position of lowest fluid potential. Hence, it is probable that injected waste with a density less than that of interstitial water would tend to remain trapped in a closed anticlinal structure (Fig. 7A), whereas waste with a density greater than interstitial water would tend to remain in a closed synclinal structure (Fig. 7B).

Faults, defined by Lahee $(\underline{12})$ as a failure along which there has been slippage of the contiguous masses against each other, offset strata and place them in contact with other older or younger beds of the same or different rock types, as shown in Figure 8. Fractured formations should not be considered for confining or disposal of wastes.

Other geologic configurations suitable for the confinement of limited volumes of liquid waste, depending on their areal extent, are sandstone lenses with both vertical and horizontal confining beds (Fig. 9) and stratigraphic traps (Fig. 10).

In addition to stratigraphy, structure, and rock properties, aquifer hydrodynamics may be significant in the evaluation of waste-injection well sites. The presence of a natural hydrodynamic gradient in the injection zone will cause the injected waste to be distributed asymmetrically around the wellbore and transported through the aquifer even after injection has ceased. Several aspects of the subsurface movement of natural fluids or injected wastes under a hydrodynamic gradient are discussed by Young and Galley (15).

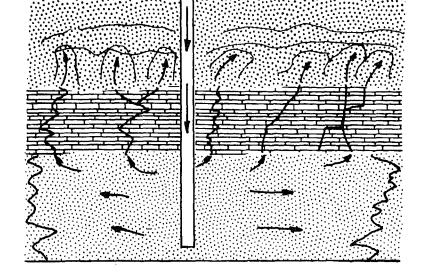
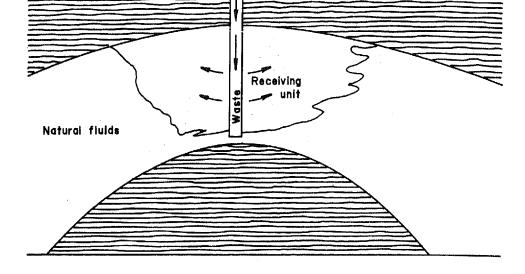
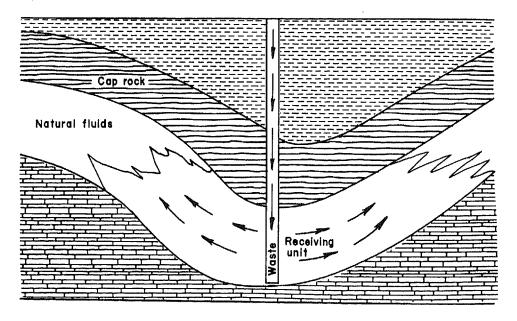


FIGURE 6 :Fluid Migrating Upward
Through a Fractured Confining
Formation.



A. - Anticlinal structure with injected liquid waste less dense than interstitial water.



B.—Syncinal structure with injected liquid waste denser than interstitial water.

FIGURE 7 .- Configurations From Folded Sedimentary Rocks.

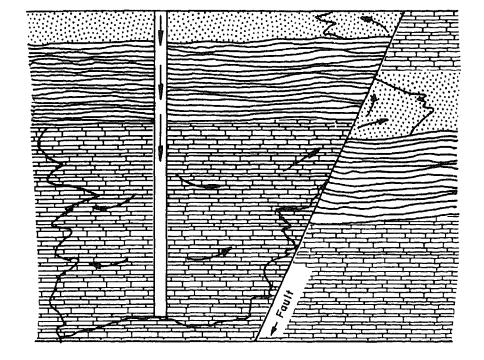


FIGURE 8 .- Faulted Formation Showing How Injected
Fluid Could be Lost to Another Formation.

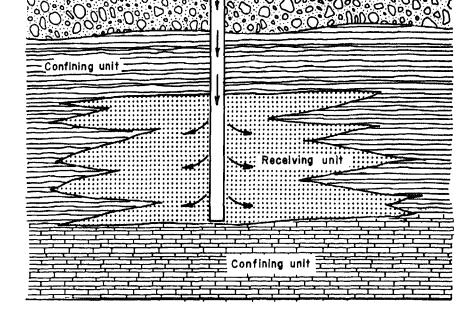


FIGURE 9 .- Sandstone Lens With Horizontal and Vertical Confining Formations.

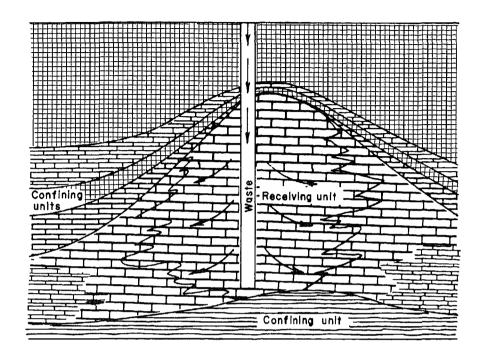


FIGURE 10 .— Stratigraphic Trap

available for waste storage by compression of the interstitial fluids (gas and brine) and the rock matrix. The reservoir pressure will gradually build to a point where continued injection would be inadvisable because of possible fracturing of the confining strata. However, of the disposal installations that were studied in detail (6), no limitations of fluid injection were experienced as a result of excessive pressure caused by fluid confinement.

Sandstone, vugular carbonate (limestone and dolomite) formations, and unconsolidated sand are the three general lithologic types that are currently being used for injection of industrial wastes.

The permeability and porosity of unconsolidated sand units cannot be determined accurately in a laboratory. These properties vary with the degree and method of compaction, and it is impossible to duplicate the subsurface conditions in a small laboratory sample.

Some consolidated sandstone formations are quite homogeneous over wide areas; thus, laboratory analyses of permeability and porosity of cores taken throughout the thickness of the formation are very useful in well completion and analysis of problems that develop later in the life of the well. The Mount Simon Formation near Gary, Indiana, is being used for injection of waste steelpickling acids, such as Wastes 16 and 17 of Table 2. The average porosity of 14.7% and permeability of 456 md are fairly consistent throughout the range in depth.

Vugular carbonate formations are difficult to evaluate in the laboratory because the vugs are so diverse in size and shape, ranging from microscopic pinholes to vugs the diameter of a pencil. The best method of evaluation is through pumping tests after well completion.

HISTORY OF AN INJECTION SYSTEM

Source and Nature of the Waste: When the plant was put into operation in 1962, two large holding ponds were constructed in an attempt to contain and evaporate the waste generated in the plant. One of these ponds was unsuccessfully used as an algae stabilization pond in an attempt to control the BOD such that the waste might be disposed of into a nearby river. Because of lack of significant solar evaporation in the area, these ponds remained

liat were under rice ourcryddion.

Prior to 1965, the manufacturing facilities were confined to the production of acetaldehyde, butanol, and other organic compounds by cracking natural gas. The waste from these operations consisted of cooling-tower and boiler-water waste containing about 1.1 wt% organic compounds (Table 4). This waste is injected into Well 1, which was completed in July 1964, at a rate between 417,000 and 576,000 gal/day.

In 1965, the plant was expanded, particularly the acetaldehyde program, and hexamethylenediamine and vinyl acetate are additional products that were included during expansion of the plant. The volume of waste from the new units (Table 5) varies from 36,000 to 280,000 gal/day. Since April 1965, this waste has been injected into a second well located 1,200 ft from the first well (9).

Geology: The wells are located near the Gulf Coast of Texas. The area is characterized by the outcrop of the Beaumont Clay. Recent alluvial deposits border the Colorado River and some of its tributaries. Immediately underlying the Beaumont Clay is the Lissie Formation, which extends to a depth of approximately 1,300 ft. These Pleistocene rocks consist predominately of sand and sandstone with intercalated shale and clay and overlie an undetermined thickness (greater than 11,000 ft) of largely undifferentiated sand, sandstone, and shale of Tertiary age. These Gulf Coast formations strike generally east-northeast and dip toward the southeast at approximately 30 ft/mile.

The interval chosen to receive the fluid waste is a well-developed persistent thick sand bed of considerable areal extent. It occurs at a depth of approximately 3,400 ft and is about 250 ft thick over several miles. Electric logs of oil exploration tests in the area indicate it to be predominantly well-sorted, fine-grained sand containing highly saline water. The interval is not productive of hydrocarbons in the region, the shallowest oil and gas production in the area being from the Frio sand at approximately 10,000 ft.

Surface Equipment: The two waste streams are treated separately, but in a similar manner. The waste from the various processes is accumulated in the process waste sump, which is a cement pit constructed low enough in the ground to take advantage of gravity drainage from the units. The composite waste is pumped from the sump to a settler-skimmer where oil and sediments are removed.

Organic Constituence, Fr.	1 000
Acetaldehyde	1,000
Acetaldol	900
Acetic acid	5,000
Butanol-1	1,300
Butyraldehyde	1,100
Chloroace taldehyde	800
Crotonaldehyde	400
Pheno1	1,200
Propionic acid	2,200
Inorganic constituents, ppm:	
Calcium	100
Iron	10
Magnesium	50
Sodium	3,000
Chloride	2,000
Sulfate	100
General Properties:	
Total hardnessppm	350
Conductancemicromhos	10,000
pH	5
Temperature° F	160
TABLE 5 Composition of waste injected into well 2, (Color: pale yellow, cloudy; odor: stale fish)	
(Color: pale yellow, cloudy; odor: stale fish)	
	500
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm:	500 600
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia	1
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia	600
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia	600 200
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol Cyclohexane Dodecane Hexanol 1-Hexylamine	600 200 100
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol Cyclohexane Dodecane Hexanol 1-Hexylamine 1,2-nexylamine	600 200 100 1,000
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol Cyclohexane Dodecane Hexanol 1-Hexylamine 1,2-nexylamine Methanol	600 200 100 1,000 1,400
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol Cyclohexane Dodecane Hexanol 1-Hexylamine 1,2-mexylamine Methanol Valeric acid	600 200 100 1,000 1,400 300
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia	600 200 100 1,000 1,400 300 200
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia	600 200 100 1,000 1,400 300 200 900 4,000
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol Cyclohexane Dodecane Hexanol 1-Hexylamine 1,2-nexylamine Methanol Valeric acid Inorganic constituents, ppm: Ammonium nitrate Sodium bicarbonate	600 200 100 1,000 1,400 300 200 900
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol Cyclohexane Dodecane Hexanol 1-Hexylamine 1,2-nexylamine Methanol Valeric acid Inorganic constituents, ppm: Ammonium nitrate Sodium bicarbonate Sodium carbonate	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia. Amyl alcohol. Cyclohexane. Dodecane. Hexanol. 1-Hexylamine. 1,2-nexylamine. Methanol. Valeric acid. Inorganic constituents, ppm: Ammonium nitrate. Sodium bicarbonate. Sodium nitrate.	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000 7,000
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia. Amyl alcohol. Cyclohexane. Dodecane. Hexanol. 1-Hexylamine. 1,2-nexylamine. Methanol. Valeric acid. Inorganic constituents, ppm: Ammonium nitrate. Sodium bicarbonate. Sodium carbonate. Sodium nitrate. Sodium nitrate. Copper.	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000 7,000 80
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia. Amyl alcohol. Cyclohexane. Dodecane. Hexanol. 1-Hexylamine. 1,2-nexylamine. Methanol. Valeric acid. Inorganic constituents, ppm: Ammonium nitrate. Sodium bicarbonate. Sodium carbonate. Sodium nitrate. Sodium nitrate. Sodium nitrate. Copper. Vanadium.	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000 7,000 80 20
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia. Amyl alcohol. Cyclohexane. Dodecane. Hexanol. 1-Hexylamine 1,2-nexylamine. Methanol. Valeric acid. Inorganic constituents, ppm: Ammonium nitrate. Sodium bicarbonate. Sodium carbonate. Sodium nitrate. Sodium nitrate. Copper. Vanadium. Manganese.	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000 7,000 80
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia Amyl alcohol. Cyclohexane. Dodecane. Hexanol. 1-Hexylamine. 1,2-riexylamine. Methanol. Valeric acid. Inorganic constituents, ppm: Ammonium nitrate. Sodium bicarbonate. Sodium carbonate. Sodium nitrate. Sodium nitrate. Sodium nitrate. Copper. Vanadium. Manganese. General properties:	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000 7,000 80 20 50
(Color: pale yellow, cloudy; odor: stale fish) Organic constituents, ppm: Ammonia. Amyl alcohol. Cyclohexane. Dodecane. Hexanol. 1-Hexylamine 1,2-nexylamine. Methanol. Valeric acid. Inorganic constituents, ppm: Ammonium nitrate. Sodium bicarbonate. Sodium carbonate. Sodium nitrate. Sodium nitrate. Copper. Vanadium. Manganese.	600 200 100 1,000 1,400 300 200 900 4,000 3,000 600 6,000 7,000 80 20

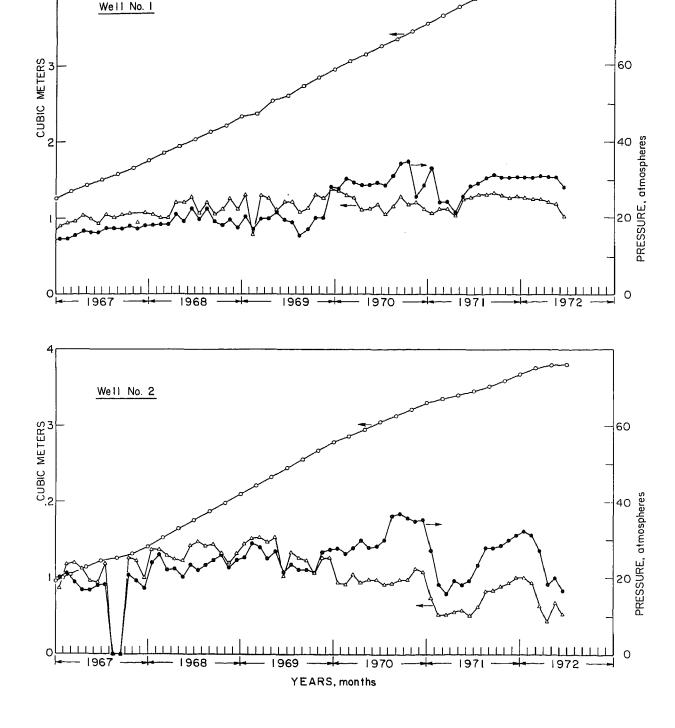


FIGURE 11. - Operating Histories of Two Injection Wells.

filtration in two stages: (1) removal of the major portion of the suspended solids with a leaf filter using diatomaceous earth precoat, and (2) final filtration with cartridge-type highpressure filters.

Two centrifugal pumps are used as needed to inject the waste from a surge tank into Well 1. Waste 2 is pumped from the setter-skimmer through two cartridge-type filters to a surge tank. Two centrifugal pumps are used as needed to inject the waste into Well 2.

Well Completion and Operation: The surface casing of the first well consists of 10 3/4-in J-55 pipe set at a depth of 1,500 ft and cemented to the surface to protect freshwater bearing sands. A string of 7-in J-55 casing is set from the surface to the bottom of the well at 3,750 ft and cemented in with a special acid-resistant cement. The injection string is 4 1/2-in fiberglass tubing that is also cemented with the special acid-resistant cement. When this tubing was installed, the joints were made up with epoxy resin to insure a good seal. Perforations were made through both casings from 3,400 to 3,600 ft. Injection was started in November 1964.

Well 2 is 2,750 ft from Well 1. The surface string in Well 2 is 13 3/8-in H-40 casing set at 1,400 ft and cemented to the surface to protect the freshwater-bearing sands. A string of 9 5/8-in J-55 casing is set from the surface to the bottom of the hole at 3,750 ft and cemented in place. This casing is perforated from 3,500 to 3,600 ft. Injection into this well was started in April 1965.

Figures 11A and 11B show the well injection histories of Wells 1 and 2, respectively. The average monthly volumes injected and wellhead pressures remained in synchronization with no abnormalities until November 1969, when an obvious increase in the wellhead pressure of both wells occurred. This is undoubtedly due to mutual interference between the wells that began in November 1969 and became progressively more pronounced as injection of fluid continued.

CONCLUSIONS

It is apparent that injection of liquid wastes into deep geologic formations can solve many difficult waste-disposal problems. However, limitations of the knowledge of how the waste

consideration in the planning stages.

The chemical and physical interactions of the waste constituents with the geologic materials at the temperatures and pressures that prevail in the subsurface environment are unknown. However, there is some evidence to indicate that adsorption and chemical reaction will retard the advance of waste constituents away from the well bore. Instead of complete volumetric displacement, the waste constituents are probably stratified behind an advancing liquid front of water containing dissolved salts not too dissimilar from the native formation brine. Accurate predictions of the migration patterns of waste constituents cannot be made until the adsorption, chemical reaction, and ion-exchange properties of each component of the waste mixture are known.

An accurate estimate of the total cost of a proposed waste-injection system can be made only when complete analyses of the waste, geologic formation, and native brine are available. A thorough evaluation of the waste must be made with respect to suspended solids, ranges of pH that promote precipitation, and chemical compatibility with the underground brine. The formation must be studied to determine the porosity, permeability, thickness, areal extent, lithology, and pore-size distribution. When these analyses are obtained, the design and cost estimate of the surface equipment and injection well can be made.

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SESSION 12

FOSSIL FUEL POWER GENERATION - ADVANCED METHODS (GASIFICATION).

Chairman: Ralph Scott

Co-Chairman: G. L. Wiesenfeld



J. A. Klein, C. H. Brown, and D. D. Lee

Oak Ridge National Laboratory

Data on the treatment of aqueous coal conversion waste are needed to ensure that water supply and quality are not adversely affected by the developing coal conversion industry. This work is not intended to develop new wastewater treatment processes, but to provide useful and timely information on the application of known control technologies to coal conversion wastewaters.

Samples of lignitic coal and steam-plant fly ash have been tested for their ability to remove polyaromatic hydrocarbons (PAHs) and refractory phenolics from aqueous streams. Removal of up to 99% of the organics was obtained with solid loadings as high as 15 mg/g. In experiments with a tapered fluidized-bed bioreactor, phenol reductions of \sim 99.9% were achieved at phenol degradation rates of 7 to 10 kg per day per m³ of reactor volume. Ozonation tests have shown that, with biologically treated wastewater, 99% of the residual phenol and 22 to 97% of the refractory PAHs, along with most of the associated colors and odors, can be degraded using ozone dosages of 0.01 to 0.14 kg per thousand liters. Experiments using wet oxidation for the destruction of both soluble and absorbed organics have been initiated. (Research sponsored by the Division of Environmental Control Technology, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.)

CONTROL ASPECTS OF UNDERGROUND COAL GASIFICATION

a. Preliminary Environmental Results of the LETC Hanna III

Underground Coal Gasification Experiment

Joseph E. Virgona, Theodore C. Bartke, and John E. Boysen

U.S. Department of Energy

Laramie Energy Technology Center

b. LLL Investigations of Ground-Water and Subsidence Effects*.
 S. Warren Mead, Francis T. Wang, and Harold C. Ganow
 Lawrence Livermore Laboratory

Changes in ground-water quality and the possible effects of subsidence and ground movement induced by the underground gasification cavity represent significant environmental concerns associated with undergroundccoal gasification (UCG). Parallel environmental studies are being conducted by the Laramie Energy Technology Center (LETC) and the Lawrence Livermore Laboratory (LLL) near Hanna and Gillette, Wyoming, respectively, to characterize these

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termined.

Their first paper (Part I) discusses the LETC Hanna III environmental studies. The Hanna III experiment (June-July, 1977) was designed primarily to provide information on the potential impacts of UCG on ground-water quality and the environmental control technology implications of those impacts. In addition, parameters critical to the process itselt were examined. Preliminary results of the ground-water monitoring during the pre-operational, operational, and early portion of the post-operational phases will be presented.

The second paper (Part II) covers ground-water and subsidence measurements carried out at the sites of two in situ coal gasification experiments conducted in northeastern Wyoming by LLL. Ground-water measurements and complementary laboratory studies have helped to clarify the environmental significance of reaction-product contaminants that remain underground following gasification. Extensive roof collapse into the gasification cavity has been documented by subsurface geotechnical measurements.

*Support for these investigations is provided by the Division of Environmental Control Technology (DOE/ASEV), the Office of Research and Development (EPA/IERL-CI), and the Division of Fossil Fuel Extraction (DOE/ASET). This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48.

ANALYTICAL STUDY OF THE EFFLUENTS FROM A HIGH-TEMPERATURE ENTRAINED FLOW COAL GASIFIER

L. D. Hansen, L. R. Phillips, R. B. Ahlgren, N. F. Mangelson, D. J. Eatough, and M. L. Lee

Bringham Young University

Effluent streams from a 100 pound per hour, pressurized, high temperature, entrained flow coal gasifier have been found to be extremely clean compared to those of other gasifiers. The water-scrubbed gaseous effluent contained only CO, $\rm H_2$, CO $_2$, $\rm N_2$, CH $_4$, and traces of $\rm H_2S$ and HCN. The gas obtained by depressurization of the scrubber water contained trace amounts of SO $_2$ in addition to these other seven gases. Polycyclic aromatic hydrocarbons, the only non-volatile organic compounds found in the scrubber water,

cerns. Statistical analysis was used to determine the effects of the process parameters: coal type, coal feed rate, reactor pressure, oxygen to coal ration, and stream to coal ratio.

Sufficient environmental control can be achieved by removing the H₂S from the gaseous effluent using an appropriate commercial process and by separating the particulate matter from the scrubber water. Particulate matter separation methods include floculation settling, froth flotation and filtration. Floculation is probably the most economical of these separation methods. Laboratory bench scale separation tests and mass balance calculations should provide valuable information as to which environmental control technology is most economically feasible.

CLEANING PRODUCER GAS FROM THE METC GASIFIER

A.S. Moore, K. Pater, C. Ray, and R.J. Belt

U.S. Department of Energy Morgantown Energy Technology Center

ABSTRACT

The Morgantown Energy Technology Center (METC) of the Department of Energy is developing a system to clean Low-Btu gas made from coal. The gas is generated in a prototype pressurized stirred fixed-bed gas producer developed in earlier work at METC that gasifies 909 Kg/hr (1 tph) of caking bituminous coal. The objective is to clean the gas to the degree needed both by any end-use system consuming the gas, and to ensure that effluents from the end-use system meet emission requirement. This report described pilot-scale development of a prototype gas cleanup system using a sidestream protion of the full 4,248,000 lit/hr (150,000 scfh) gas output from the METC gas producer. A full-flow gas cleanup system, developed as a result of the sidestream pilot-scale test investigations, is being installed and tested in phases throughout 1978. Experience with particulate, tar, light oil, and alkali removal with the side stream scrubber and experience with particulate and tar removal in the developmental testing of the full stream scrubber are reviewed.

Quench water is a principal wastewater from coal conversion processes that employ wet cleaning of gasses. The origin of the water is moisture in the coal and steam injected into the coal conversion reactor. Depending upon coal composition the quench water contains chlorides, flourides, ammonia, hydrogen sulfide and sulfur oxides. With tar producing coal conversion technology the quench water also contains cyanides, thiocyanates, phenols and various organics.

A two stage gas quenching process was proposed to absorb strong electrolytes in a small flow first-stage quench so as to improve the feasibility of reuse of the larger volume second-stage quench. A study was made to compare the technical and economic feasibility of two-stage quenching with conventional single-stage quenching.

The study evaluated methodology for estimation of quench water characteristics and engineered a concept for accomplishment of the two-stage quench. The results indicated that strong electrolytes could be absorbed from the gasses to a high degree in a first-stage quench with a blowdown of from 5 to 10 percent of the total condensate. The blowdown would be purged to waste disposal. The second-stage quench would collect 90-95 percent of the condensate containing a low content of strong electrolytes. The condensate containing weak electrolytes and organics would be treated by steam stripping and bioxidation prior to reuse as process water. Alternative disposal concepts were evaluated for two sites using representative Eastern and Western coals.

ENVIRONMENTAL CONTROL ACTIVITIES ON SLAGGING FIXED-BED GASIFICATION AT THE GRAND FORKS ENERGY TECHNOLOGY CENTER

R. C. Ellman, E. A. Sondreal
U.S. Department of Energy
Grand Forks Energy Technology Center

The 25-TPD pilot SFBG at the GFETC was reactivated in 1976 for the purpose of supporting the development and commercialization of the slagging fixed-bed gasification process. A major objective was the development of a detailed environmental assessment, including characterization of both gaseous and liquid effluents. This assessment will substantially apply both to the Hi-Btu demonstration plant currently being designed based on SFBG technology and to fixed-bed, dry-ash Lurgi gasifiers planned for first generation SNG plants.

ment and application of sampling procedures and analytical methods for characterizing gaseous and liquid effluents; 3) studies on gas cooling, separation of tar and byproducts, and treatment of waste water; 4) studies on disposal of gasifier slag and other waste solids; 5) the relation of effluent properties to gasifier operating variables, and 6) assessment of biomedical effects due to tars and waste water constituents. This report will present a summary of the assessment plan and selected data on the characterization of gaseous and liquid effluents performed to date.

OVERVIEW OF THE SYNTHANE PILOT PLANT ENVIRONMENTAL ASSURANCE PROGRAM

bу

R. P. Ladesic, R. L. Scott, and W. C. Peters U.S. Department of Energy Pittsburgh Energy Technology Center

An historical account of the development and current studies of environmental monitoring and compliance at the SYNTHANE pilot plant will be presented. This account will include the experiences and problems in establishing monitoring programs in the following areas:

Air:

Ambient Monitoring Stack Testing Fugitive Emissions Noise:

Background In Plant

Water:

Surface Water Control NPDES Sampling Continuous Water Monitoring Solid Waste:

Characterization Disposal

Occupation Health:

Problem and Direction

In February and March 1975 the first ambient air background studies were undertaken at the SYNTHANE pilot plant. Subsequent to these initial studies an environmental monitoring and compliance program was developed incorporating the areas noted above. The cost of this program to date plus facilities and equipment amount to approximately three (3) million dollars. The experience provided in interfacing with the technology development and developing the environmental monitoring and compliance program can be of value to all who are involved in small scale and large scale development.

Data on the treatment of aqueous coal conversion waste are needed to ensure that water supply and quality are not adversely affected by the developing coal conversion industry. This work is not intended to develop new wastewater treatment processes but to provide useful and timely information on the application of known control technologies to coal conversion wastewaters.

Samples of lignitic coal and steam-plant fly ash have been tested for their ability to remove polynuclear aromatic hydrocarbons (PAHs) and refractory phenolics from aqueous streams. Removal of up to 99% of the organics was obtained. In experiments with a tapered fluidized-bed bioreactor, phenol reductions of $\sim 99.9\%$ were achieved at phenol degradation rates of 7 to 10 kg per day per m³ of reactor volume. Ozonation tests have shown that, with biologically treated wastewater, 99% of the residual phenol and 22 to 97% of the refractory PAHs, along with most of the associated colors and odors, can be degraded using ozone dosages of <0.25 kg per thousand liters.

INTRODUCTION

The abundance of this country's coal resources, relative to those for crude oil and natural gas, has prompted both the Federal government and industry to undertake an intensive effort to develop processes for converting this solid form of energy into substitute gaseous and liquid fuels. Water is an essential raw material for these coal conversion processes. Process cooling is only one of the many reasons for this dependency. Often more than 30% of the energy in the coal feed is discarded as water vapor in the cooling towers. The impurities in the makeup water are discarded as wet sludges and/or blowdown streams heavily laden with contaminants. Water is also used as a source of the hydrogen needed to raise the atomic hydrogen-to-carbon ratio of coal from <1.0 to the approximate 1.5 to 3.5 values found in crude oil and natural gas, respectively. Depending on the hydrogen production process,

Research sponsored by the Division of Environmental Control Technology, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

all types of coal conversion facilities will total nearly 700 million tons/year.

Environmental and economic reasons will compel developers of coal conversion processes to maximize water reuse and to reduce pollutant levels in aqueous effluents. Because of the economic incentives favoring location of a coal conversion facility close to the mine mouth, water resources available to such a plant will be either relatively scarce and highly competed for by nonindustrial users such as farmers, municipalities, and recreationists (as in Colorado, Wyoming, Montana, North Dakota, and New Mexico), or they will be relatively abundant but heavily used by other industrial facilities (as in Kentucky, West Virginia, and Illinois). Environmental considerations aside, recovery of dissolved "pollutants" as process by-products (e.g., phenol) may become economically desirable because of raw material scarcities; however, it is difficult to justify at the present time, except for very large-scale conversion plants. Thus, ensuring the availability of adequate technology for treating the wastewaters from coal conversion processes may be as necessary a part of fostering the commercialization of a synthetic fuels industry as the development of the coal conversion technology itself.

Only recently has the development of the necessary control technology for the cleanup of coal wastewaters gained sufficient emphasis to consider its integration into the coal conversion implementation program. However, most control technology studies are considered to be add-ons for a particular coal conversion process. Unfortunately this viewpoint is often encouraged by the separation of those charged with the development of the technology from those investigating the technology available for the cleanup of aqueous streams. In many cases, judicious design of the various individual conversion process modules could allow minimal control modifications to clean up much of the wastewater problem. Given that the discharge of a wastewater stream is unavoidable, the determination of the amount of cleanup needed is a function of both present and future effluent regulations and of the proposed use of the effluent water. The development of these future regulations is presently causing a good deal of concern to those within EPA and to other investigators in the field.

2. COMPOSITION OF COAL CONVERSION WASTEWATER

Recent studies $^{2-5}$ of several coal gasification and liquefaction processes have identified the following operations as sources of wastewater: (1) separation of excess water from raw liquid products, (2) quenching and scrubbing of raw fuel gas, and (3) desulfurization and demetallization of raw liquid products. Other parts of the overall processes will provide additional sources of wastewater: (1) coal storage

wastewaters, generalizations can be formulated, depending on the type of process, operating conditions, and the nature of the coal used. The major constituents and concentrations of a representative wastewater are listed in Table 1.2 The high phenol and ammonia concentrations are typical of coal conversion process wastewaters, whether they are condensation liquors or scrubber waters. Also listed are the concentration ranges expected in future Federal regulations for a variety of components. Standards for related industries such as coking and petroleum refining were used to develop these values 2,6-7 because there are as yet no regulations for the coal conversion industry. As shown, the levels of all the components listed will far exceed the limits of the anticipated regulations.

Individual variations do exist between the component concentrations of the various wastewaters. Although these variations are not shown, they may be quite important in the consideration of specific control technologies. The presence of a significant quantity of a metallic compound, for example, could alter the effectiveness of a biological or oxidative treatment system.

A survey of the literature reveals a number of presently available and proposed technologies for the cleanup of wastewaters with compositions similar to those indicated in Table 1.2 As expected, they represent a wide range of removal efficiencies, final residual concentration levels, and costs. Efforts to obtain the relative economic costs of various environmental control technologies for the treatment of aqueous wastes from coal conversion processes have been completed. Six processes have been identified as potentially promising in this area: ozonation, adsorption, biological degradation, solvent extraction, membrane processes, and coagulation-flocculation. The economic position of the various control technologies is shown in Fig. 1 where treatment costs are plotted versus residual organic levels.

3. ORNL'S WASTEWATER TREATMENT PROGRAM

ORNL's involvement in environmental control technology consists of an assessment and screening test evaluation of the amenability of coal hydrocarbonization wastewater and other coal conversion wastewaters to various treatment technologies. As part of this program, a flow sheet was proposed that takes advantage of several available unit operations and addresses the complete treatment of coal conversion wastewaters. This processing scheme is shown in Fig. 2 and includes physical, chemical, and biological treatment of the waste stream. The unit operations that are being investigated at ORNL include the bioreactor, the adsorption

Table 1. Composition of a typical coal conversion wastewater

Component	Concentration in wastewater (µg/cm ³)	Limits of anticipated regulations (µg/cm ³)
Phenol	6,000	0.03-0.3
NH ₃	10,000	0.8 -5.0
H ₂ S	1,000	0.02-0.2
CN"	100	0.02-0.1
SCN-	500	
РАН	10	
TOC	20,000	BOD 4-30 COD 20-350

Fig. 1. Economic costs of environmental control technologies for aqueous coal conversion wastes.

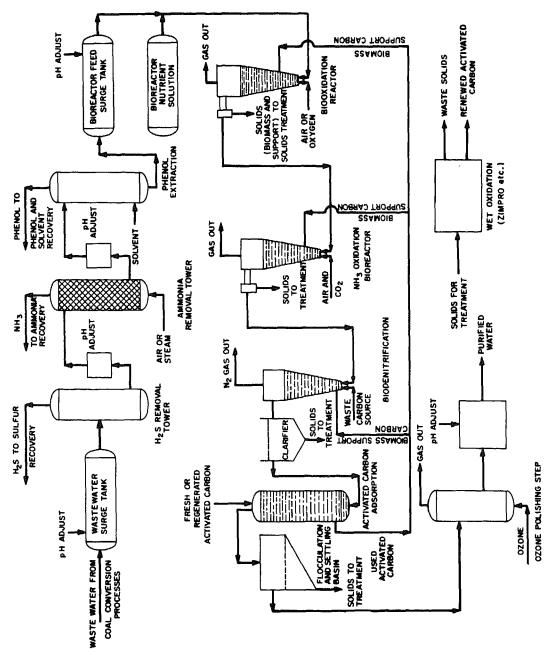


Fig. 2. Proposed integrated flow sheet for treatment of aqueous coal conversion wastes.

a commercial-scale, 30,000-ton/day SRC-I coal conversion plant producing ~3000 gal of wastewater per hour.

A tapered fluidized-bed bioreactor that has been adapted to the treatment of coal conversion wastewater is used in the biological step. This tapered fluidized-bed bioreactor system, shown in Fig. 3, consists of a tapered (2.5- to 7.6-cm) section containing a solid support to which bacteria can adhere. The solid support, which is generally a substance such as coal or sand of $\sim 30/60$ -mesh particle size, is fluidized by the flow of the waste stream to be treated. The tapered bed permits a wide range of fluidizing conditions and allows for expansion of the bed as biomass accumulates on the particles. In addition, the tapered section produces few large eddies and tends to minimize backmixing when used for two-phase (i.e., liquid-solid) systems.

The chief advantage of the fluidized-bed system is the high concentration of bacteria, which is made possible by the large surface area available on the small particles. Also, particles with excess cells can be easily removed and fresh particles added to the reactor while operation continues. In cases where oxygen is needed for metabolism, the reactor is operated as a three-phase fluidized bed and is sparged with oxygen.

The unit, which has been in operation for more than 1.5 years, has treated the aqueous waste produced by the ORNL Coal Hydrocarbonization Bench-Scale Facility. Some preliminary results indicate that the tapered fluidized-bed bioreactor in a single contacting stage can reduce the phenol and thiocyanate levels in the aqueous waste to $\leq 1~\mu g/cm^3$ and 1 to $5~\mu g/cm^3$, respectively, at rates up to 5 to 10 kg of phenol and 1.5 to 1 kg of thiocyanate per m^3 of reactor volume per day at a flow rate of 500 cm $^3/min$. In the fluidized-bed bioreactor using the hydrocarbonization scrubber water as a reactor feed, and when operated for phenol degradation, the total soluble organic content is reduced an average of 95%, whereas phenol is reduced an average of >99.5%. The concentrations of other organic components (PAHs, xylenols, etc.) are also decreased to some extent, depending on the chemical species involved and the residence time available in the reactor. 9

As a final polishing step to remove any biologically refractive compounds, ORNL is assessing the feasibility of using adsorptive materials other than expensive activated charcoal. Recent investigations have centered on synthetic resins, fly ash, and several lignitic coals. Although the ash and coals do not have the very high adsorptive capacity of activated charcoal, they generally have relatively high surface areas of $\sim\!\!250~\text{m}^2/\text{g}$, as measured with CO₂.

Both batch sorption tests (isotherm tests) and column screening runs have been performed. In the batch tests, 40 ml of the waste solution and

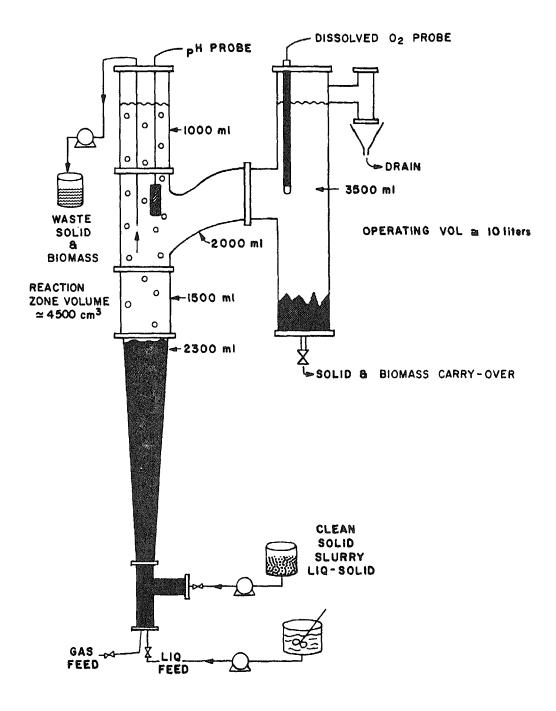


Fig. 3. Schematic drawing of the tapered fluidized bed bioreactor system.

in some of these resins; however, the 4-hr results were not included due to insignificant adsorption.

Column screening tests have recently been performed with two Texas and one North Dakota lignite coals on synthetic wastewater and actual wastewater from the ORNL Coal Hydrocarbonization Facility and a coal tar chemical plant. For the synthetic solutions, both naphthalene and phenanthrene were used as representative, but noncarcinogenic, PAH.

These tests were performed in a packed bed consisting of a 50-ml burette loaded with $\sim\!33$ g of coal and operated in the upflow mode. The results of one series of tests are shown in Table 3. Because column breakthrough was not reached in most cases, the contaminant loadings reported in Table 3 are minimum values.

Ozonation, an attractive choice for a final cleanup step, is being investigated. In this case, ozonation, normally considered an expensive choice for effluent cleanup, would be used to destroy only those refractory materials that pass through biological treatment. For these screening tests, a small batch ozone reactor was used to treat ORNL biotreated coal hydrocarbonization scrubber water. This system, shown schematically in Fig. 4, consists of a corona discharge ozone generator with a maximum output of 4.5-g/hr, a 1.2-liter reactor, impingers for ozone concentration determination, and a flow-through fluorescence detector. The flow monitor is used to continually follow changes in native fluorescence, which is a gross indicator of the relative abundance of polynuclear aromatic material (PAH). Samples are extracted periodically and analyzed for total organic carbon and phenolic content.

Some preliminary results indicate that ozonation can reduce the phenol and PAH levels in the aqueous wastes to $\leq 0.1~\mu g/cm^3$ and $\leq 0.25~\mu g/cm^3$, respectively, with contact times of 15 min or less. In the ozone reactor, the phenol and PAH levels were reduced by 95 to 98%. Optimum operating conditions appear to be 20 to 35°C; pH, 11.2; gas flow, $\sim\!0.3$ liter/min; and inlet ozone concentration, 70-150 mg ozone per liter of oxygen. Outlet ozone concentration and fraction ozone utilized were not measured. The effects of flow rate, pH, and temperature on rate of fluorescence decrease are shown in Figs. 5 to 7.

4. ONGOING WORK

The objective of our present work is to characterize the effectiveness of the various treatment systems for the cleanup of aqueous coal conversion wastes. Since a number of these concepts are still in the developmental stage, an integrated procedure has been formulated to test

	Naphti (p	nalene om)	Anthra (ppr		Benzanti (ppr		Phenan (ppr	
Sorbent	0.3	3.0	0.0375	0.075	0.002	0.01	0.232	1.16
Activated carbon, 1 mg 4 hr 16 hr	0.79 0.88	0.78 0.96	0.73 0.87	0.50 0.90	0.88 0.94	0.90 0.95	0.91 0.90	0.43 0.77
Resins, 16 hr								
Chelex 100, 1 g	0.69	0.22						
IR-120, 1 g		0.58					0.78	0.93
IRA-400, 1 g 0.1 g	0.83 0.40	0.92 0.41	 1.00	0.97	1.00	0.90	1.00 0.97	1.00 0.84
AG-MP-50, 1 g			0.80	0.75			1.00	0.92
Ash, 1 g, 4 hr								
John Sevier fly ash		0.68						0.93
Kingston fly ash		0.78						0.96
Wyodak hydro- carbonization ash		0.59					~ -	0.89

Hydrocarbonization wastewater

Phenol 4.0 (ppm) Total carbon (107 ppm)

Texas lignite 1 g, 3 hr

0.20

0.10

Adsorption of contaminants from wastewater in a packed column^a Table 3.

Sorbent	Solution tested	Concentration (ppm)	Flow rate (m&/min)	Coal loading (mg/g coal)	Ren (
North Dakota lignite	Naphthalene	3.0	0.9	1.6	_
Texas lignite	Naphthalene	3.0	5.0	2.2	~
North Dakota lignite	Phenanthrene	1.16	5.0	1.0	
Texas lignite	Phenanthrene	1.16	1.2	0.4	(
Texas lignite	Phenol	200	0.9	2.1	~
Texas lignite	Phenol	20	1.2	7.8	·
North Dakota lignite	Coal tar Wastewater	55 ^b	1.2	0.8 ^b	
Amberlite XE-348 carbonaceous resin	Phenol	200	9	112	5
ORNL hydrocarboni- zation char	Pheno]	200	9	0~	•
Texas Wilcox lignite	Hydrocarboni- zation water	107 ^d 4 ^e	1.3	1.5 ^d 0 ^e	•

aAll tests run in a standard 50-m2 burette with ∿33 g of sorbent. bTotal carbon. cPolynuclear aromatic hydrocarbon. dTotal organic carbon. ePhenol.

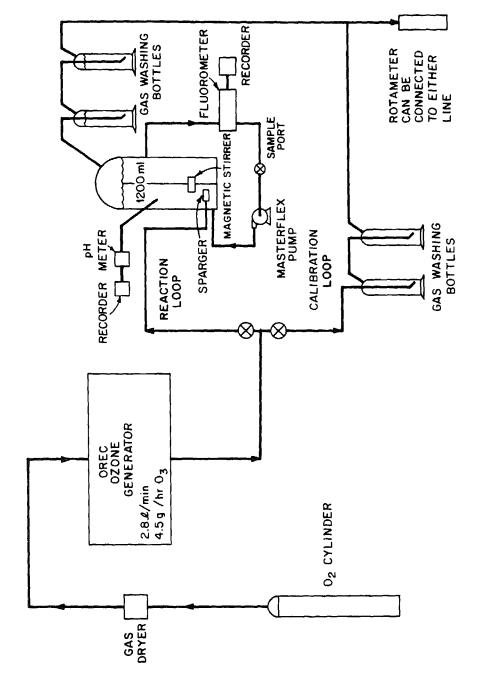


Fig. 4. Schematic drawing of batch ozonation system.

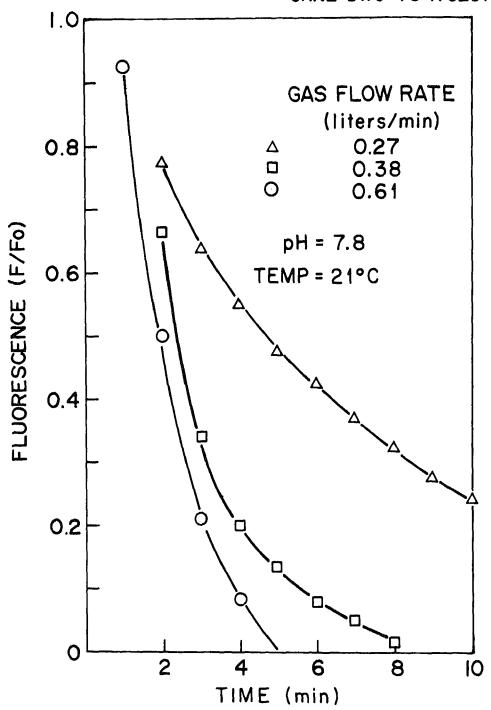


Fig. 5. Ozonation of hydrocarbonization was tewater. Effect of gas flow rate.

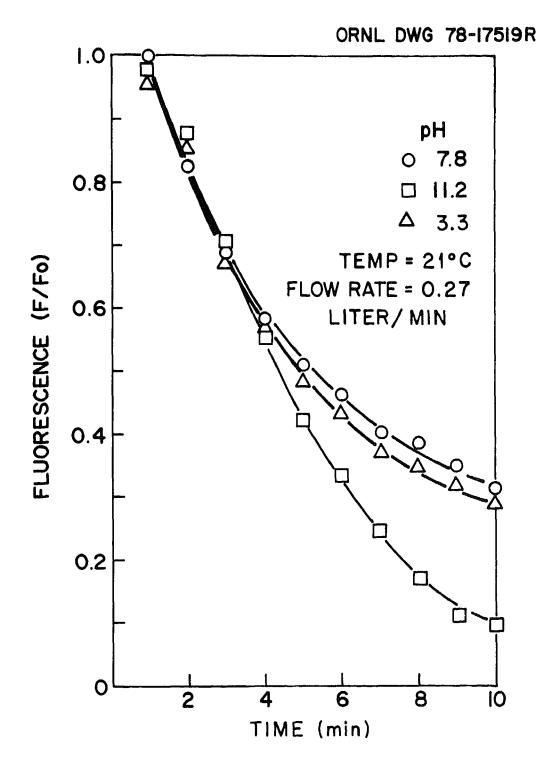


Fig. 6. Ozonation of hydrocarbonization wastewater. Effect of pH.

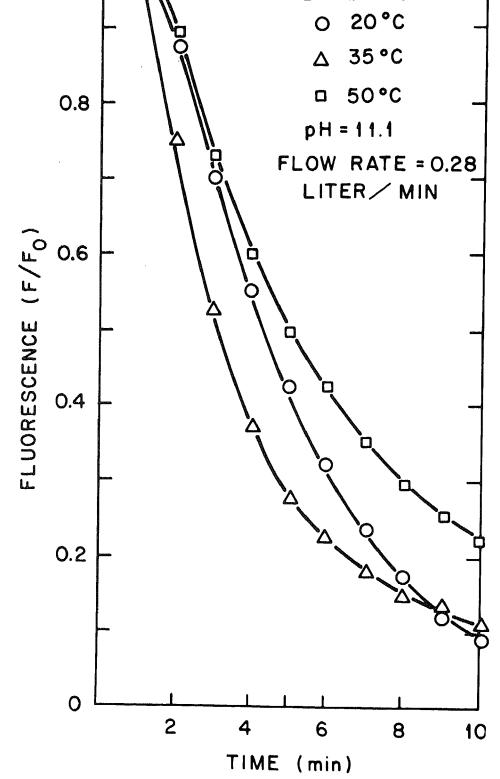


Fig. 7. Ozonation of hydrocarbonization wastewater. Effect of temperature.

for characterizing the efficiency of environmental control methods for any coal conversion effluent. For the initial effort, untreated, biotreated, and fully treated material from ORNL's hydrocarbonization experiments will be analyzed, fractionated, and tested for both acute and mutagenic toxicity.

Future studies will continue to concentrate on removing toxic organic and carcinogenic compounds. However, additional work will include integrating the individual cleanup methods into a complete cleanup system similar to the one shown in Fig. 2.

CONCLUSIONS

Although several gasifiers are being developed that are theoretically capable of being operated under conditions in which they should produce little, if any, aqueous discharge, most of the developing coal conversion processes will produce large quantities of effluents. Because any sour gas cleanup or wet scrubber will transfer pollutants to a water stream, aqueous discharges will be of great concern and will contain sizeable amounts of known toxic and carcinogenic compounds. Present standards do not call for specific levels of treatment; however, future standards will surely be more stringent and will mandate extensive control technology.

The screening of a number of available control technologies has demonstrated that a combination of control technologies can conceivably be used to produce an acceptable effluent water stream. To date, however, these technologies have not been tested on actual wastewater in the field. Several coal conversion processes are presently being considered for demonstration-level projects. If indeed the purpose of these projects is to demonstrate the commercial feasibility of these processes, then it should also be desirable to demonstrate their environmental acceptability.

Wastewater processing trains incorporating some of both presently available and advanced techniques should be constructed and used to treat various coal conversion wastewaters. Although it is not practical to design these pilot treatment processes to treat all the wastewater from any of the various demonstration plants, they should provide data on the treatability of actual wastewater streams and allow evaluations of the various technologies.

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ABSTRACT

Since 1972 the Laramie Energy Technology Center (LETC) has been seeking an economically viable process for gasifiying coal underground (1-7). The LETC has been investigating the potential environmental impacts associated with underground coal gasification (UCG) at four UCG test sites near Hanna, Wyoming (8-10). The Hanna III experiment (5-7) was designed to provide information on the potential impact of UCG on groundwater quality and the environmental control technology implications of those impacts along with parameters critical to the process itself. Environmental objectives were: (1) to characterize the pertinent aquifers, (2) to determine preoperational water quality in the aquifers, and (3) to assess the impacts of UCG on groundwater quality.

INTRODUCTION

The first United States field test of in situ or underground coal gasification (UCG) were started in 1947 by the U.S. Bureau of Mines (11-14) at Gorgas, Alabama and lasted through 1958. The overall results of these tests were disappointing because seam thickness and coal type were not favorable for UCG. In addition, the economic climate was poor because of the availability of large quantities of cheap oil and natural gas.

Gulf Research and Development Company (15) conducted a small test in western Kentucky in 1968. The test produced a very high heating value product gas for an air injection system, but the reaction was limited to devolatilization. The test also showed that air injection pressures above overburden pressure could be used to enhance the permeability of the coal seam.

The current U.S. program was developed in the early 1970's, but differs from the earlier programs in being highly instrumented, modeled, and analyzed. This program addresses coals of different ranks, geographical areas, angles of dip, operational techniques, and product gas utilization. All processes under development are designed to complement surface technologies and recover the resource that is either too thin, deep, or steeply dipping for the conventional recovery methods.

with the WCT Program divided into the Western Low Btu Gas/Air (WLBG) and Western Medium Btu Gas/Steam-Oxygen (WMBG) Projects.

The WLBG Project (1-10) has been conducted by the Laramie Energy Technology Center (LETC) since 1972 near Hanna, Wyoming. The LETC has developed the Linked Vertical Well (LVW) linkage process to increase the permeability of the coal seam. Sandia Laboratories has provided instrumentation and monitoring to LETC since 1974.

The WMBG Project (16-21) has been conducted by the Lawrence Livermore Laboratory (LLL) at Hoe Creek, Wyoming in the Powder River Basin since 1975. LLL has increased the permeability of the coal seam by explosive fracturing, LVW, and deviated borehole drilling.

The ECT Project (22) which is investigating methods of in situ gasification of near market, swelling coals is directed by the Morgantown Energy Technology Center (METC). The CO-Flow Stream Concept developed by METC is planned for field testing in FY 1980 either at its Princetown, West Virginia test site or at an alternate test site yet to be determined.

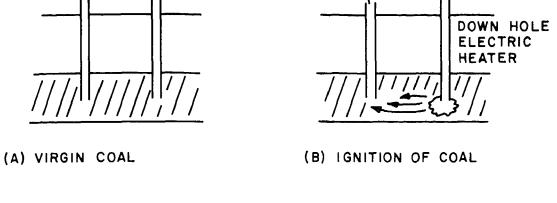
The SDB Technology (coal seams greater than 35 degrees relative to the earth's surface) is being developed by Gulf Research and Development Company near Rawlins, Wyoming, through a DOE contract (23). This first phase of this project (site selection, characterization, and preliminary design) has been completed, and the first field test is planned for late FY 1980.

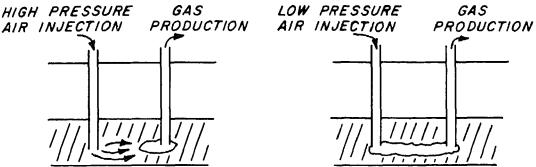
There are also some active privately funded UCG projects, but they will not be discussed in this paper.

An integral part of the technology development is a program to determine the potential environmental impacts associated with UCG and the control technology that may be needed not only to meet State and Federal environmental regulations but also for end product utilization. This paper will discuss portions of the environmental programs (groundwater and subsidence) associated with the WLBG and WMBG projects.

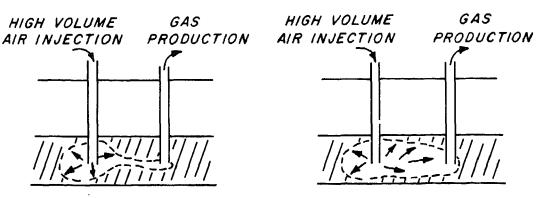
The LETC has been investigating the potential environmental impacts associated with UCG at its four UCG test sites near Hanna, Wyoming, (Figure 1) on land made available by Rocky Mountain Energy Company (a subsidary of Union Pacific Railroad). Complementary studies are also being conducted on other types of coal and seams (18-21). Three primary environmental concerns associated with UCG are:

- 1. Effluent gas quality
- 2. Surface and subsurface water quality
- 3. Subsidence effects





- (C) COMBUSTION LINKING FRONT PROCEEDS TO SOURCE OF AIR
- (D) LINKAGE COMPLETE WHEN COMBUSTION ZONE REACHES INJECTION WELL (SYSTEM READY FOR GASIFICATION)



- (E) COMBUSTION FRONT
 PROCEEDS IN THE SAME
 DIRECTION AS INJECTED
 AIR
- (F) COMBUSTION FRONT EVENTUALLY REACHES PRODUCTION WELL

Figure 1. LVW Process Description

sustain the fire which moves toward the oxygen source, contreteditent to the air flow. As the fire proceeds, carbonization of the coal produces volatiles and leaves a highly porous, permeable pathway between the wells (D). This preparation process, known as reverse combustion linking, is necessary since virgin coal generally does not have sufficient permeability to allow the high air injection rates needed for efficient gasification. Upon completion of linking, high volumes of air are injected at low pressure (E), expanding the combustion zone towards the initial ignition well where the gases generated during linking and gasification are recovered. This expansion generally has a spherical geometry with some distortion toward the production well due to the presence of the linkage pathway. The expansion of the gasification proceeds at a rate of about 1 to 2 feet per day and grows in width up to two-thirds of the well spacing by the time the front reaches the production well. This results in efficient utilization of the coal between the two wells as shown in (F).

The combustible gases produced are hydrogen, methane, carbon monoxide, ethane and propane. Nitrogen and carbon dioxide are also produced, but have no heating value and dilute the product gas. The process yields 120 to 185 Btu/scf gas. This low-Btu gas can be economically produced (24-26) and efficiently used in a gas-fired turbine or a gas-fired steam boiler to produce electric power.

The Hanna III experiment (5-7) was conducted for approximately seven weeks during June and July 1977. About 2800 tons of coal were gasified during the 38 day gasification period with production rates of up to 10 MM scf/day. The average heating value was 138 Btu/scf with an average thermal efficiency of 78 percent for gasification. Water was added to several of the wells during the gasification phase.

HANNA III OBJECTIVES

The primary objective of the Hanna III experiment was to study the effects of an UCG process on associated aquifers. Three sources of ground-water degradation appear possible. One potential source of degradation results from large amounts of water being removed from the coal as steam with the product gas. This causes the remaining groundwater to carry on increased salt load. Another source of degradation comes from the thermal degradation or transformation of mineral matter within and around the coal seam, with influxing groundwater leaching inorganic salts from these materials thus increasing the inorganic salt load. Organic byproducts produced during carbonization of the coal are swept to the surface with some being left behind as a third source of groundwater degradation. These liquid by-products consist principally of pyridines, phenols, and neutral aliphatic and aromatic hydrocarbons. Any of the organic materials left in the underground system might eventually be dispersed throughout the groundwater regime where communication exists.

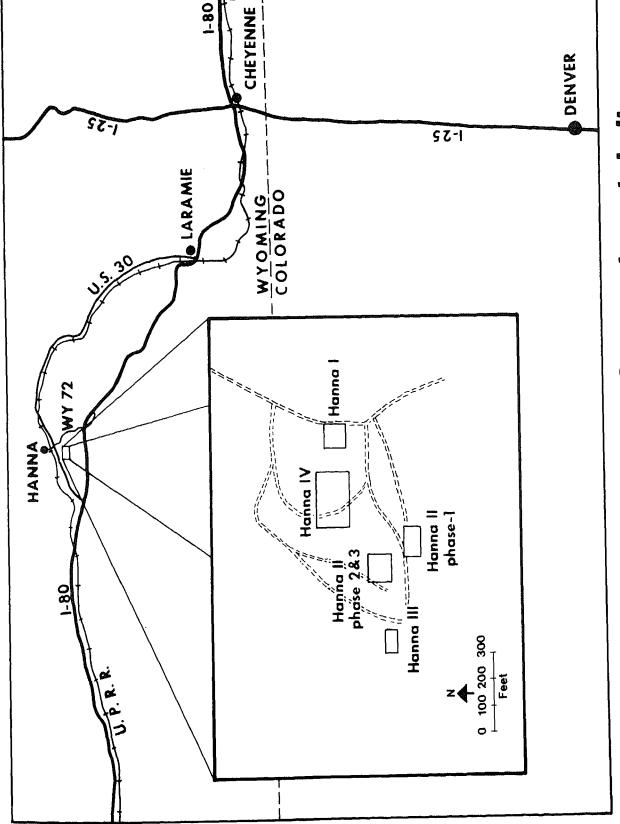


Fig. 2 - LETC's UCG experimental sites

primarily being conducted to allow determination of necessary environmental control strategy, several parameters critical to the process itself were also examined. Table I lists the specific objectives of the Hanna III experiment.

EXPERIMENT

The Hanna III experiment can be divided into three phases:

- 1. Preoperational (Baseline) Prior to Julian Day (JD) 157,
- 2. Operational JD 157 through 211, and
- 3. Postoperational after JD 211

with the operational phase divided into three stages:

- a. Start-up JD 157 through 162,
- b. Linkage JD 162 through 173, and
- Gasification JD 173 through 211.

Twelve monitor wells were strategically placed within and downdip from the gasification test area (Figure 3). Wells 1 and 2 were the process wells; wells 3, 4, 5 and 14 were monitor wells for the upper aquifer; and wells 6-13 were monitor wells for the coal seam.

Preoperational monitoring of aquifer characteristics and baseline ground-water quality was conducted. Upon completion of this initial characterization work, wells 1 and 2 were linked by reverse combustion, followed by gasification from well 1 to well 2. During the test, temperature, hydrostatic pressures, and electrical conductivities were continuously monitored in each of the monitor wells. (Continuous monitoring of these parameters were planned during the postoperational phase, but the postoperational burn zone conditions have made these probes inoperable and were subsequently removed). The temperatures and pressures yielded data on water level and temperature changes as a function of both time and process parameters.

Three sets of water samples from each of the fourteen wells in the Hanna III pattern plus three sets from Corehole #4 near the Hanna II site (a well cased and completed to the Hanna #1 seam approximately 800 feet NNE of the Hanna III site) were collected, fractionated, and analyzed, prior to the test. Table II shows the components for which analyses were performed and the fractionation and preservation techniques used. Selected samples were analyzed for the organic constitutents by GC-MS (Gas Chromatography-Mass Spectroscopy).

The well pattern was also designed to obtain the permeabilities and porosities (transmissivities and storage coefficients) and the continuity and directional nature of both the coal seam aquifer and the overlying aquifer. Data on drawdown and pressure build-up tests were obtained by pumping wells 10 and 1 (in turn) for the seam and well 3 for the overlying aquifer.

HANNA II OBJECTIVES

PROCESS

- TEST PROCESS CONTROL TECHNIQUES
- DEMONSTRATE PRODUCTION OF CONSTANT HEATING V PRODUCT GAS BY CONTROLLING THE AIR:WATER RATION THE GASIFICATION ZONE
- IMPROVE THE MATHEMATICAL MODEL

ENVIRONMENTAL

- 1. CHARACTERIZE THE PROPERTIES OF THE COAL SEAM AQUIFER AND OF THE OVERLYING AQUIFER
- **DETERMINE PRE- AND POST-EXPERIMENT WATER QUALI BOTH AQUIFERS**
- ASSESS THE IMPACTS OF UCG ON GROUNDWATER QUAL

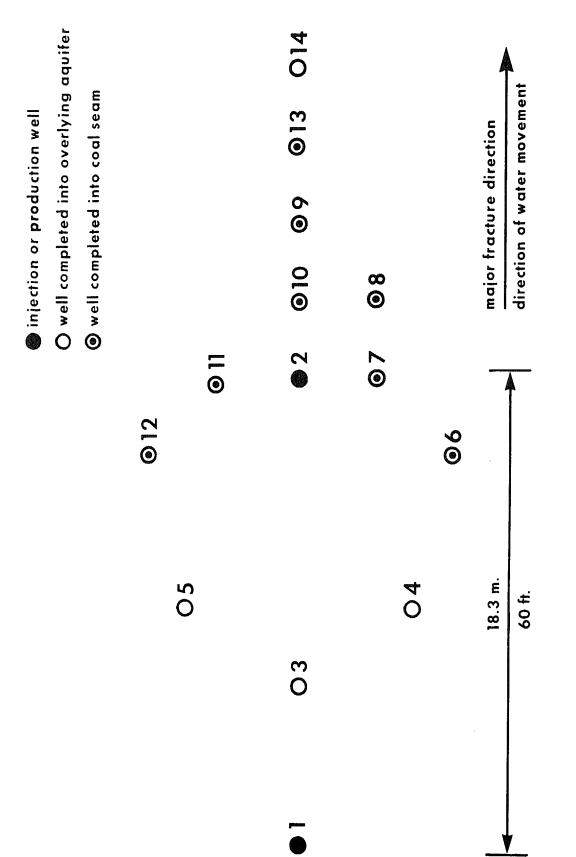


Figure 3. Hanna III

FRACTION	PRESERVATION TECHNIQUE	ANALYSIS
H	COOLED TO 4°C	SO4 [±] , HCO3 [±] , CO3 [±] Si, TDS, TOC, B, TOTAL P, F ⁻ , CI ⁻ , TOTAL INORGANI CARBON
Ħ	1:8 HNO3	Na, K, Ca, Mg, Cd Pb, Zn, Fe, Al, Cu Mn, Mo, Ti, V, As,
目	1:10 H ₂ SO ₄	NH3-N, TOTAL N, NO2-N, NO3-N,
Ħ	CONC. HNO ₃ 5% (w/w) K ₂ Cr ₂ O ₇	ħ
K	0.1 M Zn(C2H3O2)2	"S

TABLE II: Hanna III Fractionation and Preservation Techniques

(18-24 months) to determine adsorption rates as a function of time and distance from the source, the extent of the interconnection between the two aquifers, and the groundwater quality changes resulting from migration of leached species.

RESULTS AND DISCUSSION

Preoperational

The initial results of the analyses from the 14 wells at the Hanna III site and from Corehole #4 indicated that the waters contain predominantly sodium bicarbonate. The preoperational samples from the wells at the Hanna III site can be differentiated on the basis of total dissolved solids (TDS) levels and well location, i.e., in the coal seam or in the overlying aquifer. A comparison of some water quality parameters of the two groupings is given in Table III. The samples taken from the coal seam show considerably higher TDS levels and higher concentrations of sodium, bicarbonate, and sulfate.

The composition of these waters was such that they produced a high sodium absorption ratio, which would render them unacceptable for irrigation. The residual sodium carbonate levels were also high and indicated alkali problems would develop if this water were used for long-term irrigation. quality of the water in the overlying aquifer is compared to the proposed Wyoming Department of Environmental Quality (DEQ) groundwater quality regulations (27), it meets most of the requirements of a Class V water (is or has the potential for being used as livestock water), but the high concentrations of fluoride and mercury may lower this groundwater to a Class VI (is or has the potential for being beneficially used) or Class VII (the potential for beneficial use shall be determined). The quality of the coal seam aquifer meets the DEQ requirements for a Class III water (has the potential for being used as domestic water), but again the fluoride and mercury concentrations may reduce the groundwater to a Class VI or Class VII. Preliminary results of the organic analyses by GC-MS showed that only one sample (Well 13) contained extraneous organic compounds (28).

Pre-operational drawdown tests showed that the two aquifers were not connected. The undisturbed water level in the coal seam was 120 ft. from the surface while the upper aquifer had water 95 ft. from the surface. Thus, the two zones could be tested independently of each other. The calculated axis of major permeability in the Hanna III site lies 82° east of north. The average permeability for the seam is about 5 md, but the zone is heterogeneous. The upper zone exhibits an even more marked directional nature or heterogeneity, but its average transmissibility is about the same as that of the coal seam (29).

TABLE III

Comparison of the wells at the Hanna III site (all values reported as mg/l, with the average given first, followed by the range found)

Parameter	Group 1a	Gro
TDS (@180°C)	1224 (992-1450)	2614 (18
Sodium	496 (238-625)	1107 (75
Carbonate	33 (0-181)	25 (0-2
Bicarbonate	1131 (799-1280)	1774 (12
Sulfate	35 (1-143)	679 (244
Total Inorganic Carbon	224 (204-248)	364 (328
Fluoride	1.8 (1.0-3.2)	1.04 (
Ammonia (as N)	1.1 (.9-2.1)	1.7 (1
Boron	0.03 (<0.01-0.11)	0.08
Total Organic Carbon	41 (31-51)	11 (9-1

^a Wells 1, 2, 6, 7, 8, 9, 10, 11, 12, 13 and Corehole 4.

^b Wells 3, 4, 5 and 14. (Overlying Aquifer)

but responses were observed during gasification. Well 3 responded first, as expected, and within ten days responses were observed in the other wells completed into the overlying aquifer.

The temperature remained constant (45-55°F) during the start up and linkage phase. During gasification temperature increases of about 50°F were observed at wells 6 and 12 from JD 178 to 200, and then at wells 7, 10, and 11 from JD 200 to 204. No temperature changes were observed at wells 8, 9, and 13. This sequence of well response follows the gasification progression from well 1 to 2. (There were no coal seam thermocouples to track the burn progression as in the other Hanna experiments.) Temperature increases in the overlying aquifer (well 3) were observed on JD 198 (Figure 4) which indicated breakthrough into the aquifer. No temperature responses in the other wells were observed.

The conductivity probes indicated changes in loading level in wells 9 and 13 during start up. This response probably resulted from the ignition and air injection into nearby well 2, and the production gases following a more permeable zone leading towards wells 9 and 13. During the link, the conductivity of the water in the coal seam aquifer remained constant, and during start up the conductivity of the overlying acquifer remained constant. It is apparent from both the previously discussed linkage temperature data and this conductivity data that the linkage path did not intersect or come close enough to the temperature or conductivity probes to generate a response.

During gasification conductivity responses were observed within the first five days at wells 9 and 13. These wells were also the first to show conductivity responses during start up. Production gases from the gasification zone probably again followed a more permeable zone to these wells. Well 10 located between wells 2 and 9 responded on JD 203. Wells 7, 8, and 11 remained constant. Increased conductivity levels were observed at well 3 in the overlying aquifer on JD 187 (Figure 4) indicating product gas seepage into the overlying aquifer. Wells 14 and 4 responded approximately five days later, but well 5 remained constant. (Anemolies were observed in the well 5 probes since they were installed).

Hydrostatic pressure, conductivity, and temperature responses at well 3 were observed on JD 184, 187, and 198, respectively. The pressure response indicated that there was communication (fissures and coal shrinkage) between the coal seam and the overlying aquifer. As the gasification cavity increased in size and overburden sluffing continued, additional fractures penetrated into the overlying aquifer allowing product gas into the aquifer resulting in conductivity increases. Finally, on JD 198 additional roofall caused communication between the gasification zone and the overlying aquifer.

Wells 6 and 12 showed opposite temperature and conductivity responses. The temperature increased, remained constant for three weeks (JD 178-200), and returned to its original level. Three days later the conductivity probes

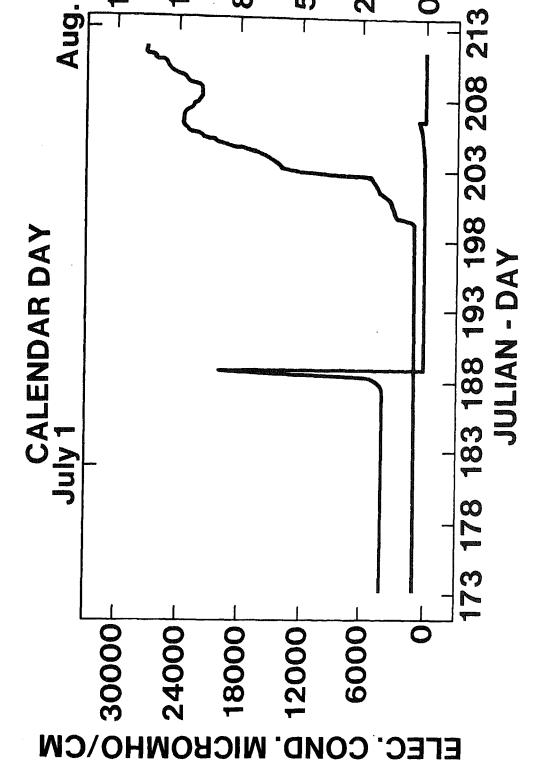


Fig. 4 - Downhole Conductivity and Temperature Responses for Well #

Postoperational

Early postoperational hydrostatic pressure, temperature, and conductivity data have not been analyzed and interpreted due to computer data retrieval problems. This data will be retrieved and analyzed in the near future.

Preliminary results from the first month's postoperational water quality monitoring appear to indicate that the sulfate and chloride concentrations are decreasing and sodium and total dissolved solids are increasing in all wells. Organic characterization data are not yet available.

CONCLUSIONS

Preoperational water quality data indicates that the natural groundwater would be unacceptable for short and long term irrigation, and when the quality is compared to the proposed Wyoming Department of Environmental Quality Groundwater Regulations, it may only meet the requirements for a water that has the potential for beneficial use.

Preliminary results indicate that UCG does have an impact on the ground-water. As the monitoring program and data analysis and interpretation progresses, the extent of the environmental impacts will be determined. Once these impacts are known, control and/or utilization technology will be determined.

ACKNOWLEDGEMENTS

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ABSTRACT

The conversion of coal into combustible gases promises to become an important method of coal utilization. If this conversion is carried out with the coal in place underground - in situ coal gasification - additional environmental and economic advantages can be realized. Our investigations are designed to evaluate some of the environmental implications of this alternative energy technology, and to identify appropriate environmental controls.

Changes in ground-water quality and the possible effects of subsidence and ground movement induced by the underground gasification cavity represent significant environmental concerns associated with the in situ gasification process. We have measured these effects at the sites of two in situ coal gasification experiments conducted in northeastern Wyoming by the Lawrence Livermore Laboratory. Our measurements of ground-water quality in the vicinity of the gasification experiments indicate that the reaction products, such as ash and some coal tars, that remain underground following gasification, are a potential source of localized ground-water contamination. However, the concentration of important contaminants, such as phenols, show a significant decrease due to adsorption by the surrounding coal. Complementary laboratory measurements are providing detailed information concerning this adsorption process.

We have also conducted laboratory and field measurements, in conjunction with modeling studies, to evaluate the effects of subsidence phenomena. Data from subsurface geotechnical instruments installed at the second gasification experiment, as well as measurements of ground-water levels, indicate that roof collapse connected the gasification cavity with overlying aquifers. The environmental implications of this interconnection are being investigated. Our results suggest that hydrogeological site-selection criteria may be of considerable environmental importance in choosing locations for commercial-scale operations.

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the gasification of coal is accomplished with the coal in place underground in situ gasification - additional environmental and economic advantages can be realized. For example, in situ coal gasification can be carried out without the need for underground mine workers, and it may make recovery of very deep coals economically attractive.

In situ coal gasification generally involves a complex series of chemical reactions, but it can be simply characterized as the heating of coal in the presence of gasifying agents such as oxygen and steam. Some of the coal is burned to provide heat to drive the gasification reactons. In the simplest form of in situ gasification, two or more process wells drilled into the coal seam are used, after the coal is ignited, to inject air or other gasifying agents and to withdraw the resulting combustible gas mixture (Fig. 1). In most cases, the coal's permeability must be enhanced, before gasification, along a path connecting the process wells. (The need to achieve this preliminary connection reliably and economically represents an important current challenge in the development of a practicable in situ technology.) The product gas generally requires some form of clean-up in a surface plant and, if synthetic natural gas is the desired product, an upgrading process to achieve higher energy density.

Although in situ coal gasification offers important environmental advantages when compared with more conventional methods of coal utilization, there are significant environmental concerns that need to be investigated. If these concerns are addressed now, in parallel with the development of the in situ method, it will be possible to identify appropriate control technologies in a timely manner and, perhaps, influence process development such as to preclude or minimize adverse environmental effects.

In order to insure that realistic and effective control methods will be identified, it is essential to develop a quantitative understanding of potential environmental effects as they would occur in connection with large, commercial-sized operations. Some of these possible effects are peculiar to underground gasification and have not been previously investigated in detail. Futhermore, important environmental consequences may require decades to develop. We are therefore concentrating our present efforts on the accumulation of basic data concerning the potential sources of environmental effects, and on the development of reliable, predictive modeling capabilities. With this background, it should be possible to isolate control technologies that are realistically applicable to this promising method of coal recovery.

Two characteristic features of the <u>in situ</u> coal gasification process have led to particular environmental concern: first, the fact that some of the reaction products remain underground as potential ground-water contaminants and, second, the cavity (and possible subsidence) produced by the extraction of the gasified coal. Our <u>in situ</u> coal environmental group at the Lawrence

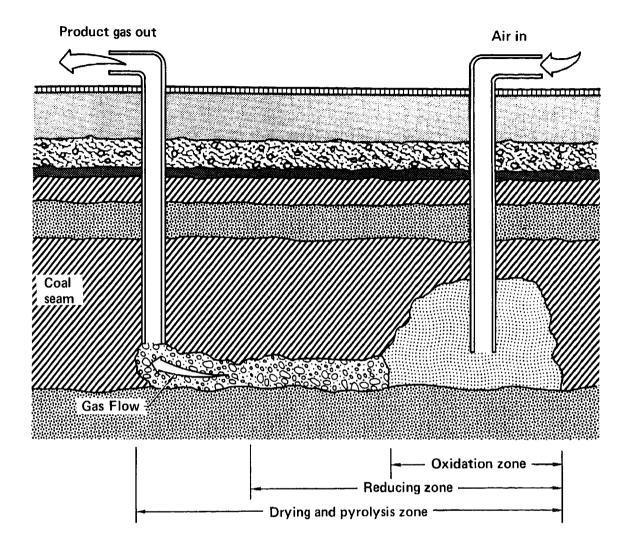


Figure 1. Schematic representation of the *in situ* coal gasification process. The region ahead of the oxidation zone has been modified before gasification to provide a path of increased permeability that will permit adequate gas flow.

in situ gasification experiments, laboratory investigations, and predictive modeling studies.

LLL has conducted two <u>in situ</u> coal gasification experiments 1,2 at its Hoe Creek site in northeastern Wyoming. These experiments have given us the opportunity to measure changes in ground-water quality and subsidence effects associated with two underground gasification operations.

The Hoe Creek site is located in a sparsely populated region of gently rolling semi-arid rangeland. This area is part of the Powder River basin of northeast Wyoming and southeast Montana - a region that may contain half a trillion tons of coal suitable for in situ gasification. The coal gasified in the Hoe Creek experiments (the Felix II Coal) is 25 ft thick and lies at a depth of about 125 ft - well below the static water level. The Felix II Coal is an aquifer and is overlain by two additional aquifers. A detailed evaluation of the hydraulic characteristics of the Felix Coal and the nearby strata at the Hoe Creek site will be found in reference 3.

The first Hoe Creek experiment took place in the fall of 1976. The two process wells - for injecting air and extracting product gas - were about 33 ft apart, and chemical explosives were used to produce enhanced permeability in the Felix II coal. Approximately 120 tons of coal were gasified in an 11-day experiment.

A second experiment, Hoe Creek II, was conducted during the fall and winter of 1977. The process wells were located approximately 60 ft apart and the required path of enhanced permeability was achieved using a preliminary "reverse combustion" technique, developed in this country by the Laramie Energy Technology Center. The gasification operation lasted 58 days, during which approximately 2000 tons of coal were converted to gas and extracted through the production well. The average energy content of this gas was 108 Btu/scf. Gas losses during this experiment averaged 20%.

Perhaps the most significant environmental concern associated with the underground gasification of coal stems from the existence of gasification reaction products that remain underground. These residual materials include coal ash, char, some of the coal tars, and approximately 10-15% of the product gases which are not extracted through the production wells. When ground water returns to the gasification zone, the ash is leached, producing inorganic contaminants, and some of the other residual materials, including organics are dissolved. The contaminated water moves through the coal seam in the general direction of the natural ground-water flow. Fortunately, there are other natural phenomena - for example, the filtering and adsorption properties of coal itself - which tend to purify the ground water and to restrict the contaminants to a localized region. Nevertheless, the ultimate environmental significance of the residual underground products is not yet known.

The ground movement and potential subsidence associated with the creation of a gasification cavity are also of significant environmental concerning part, because these phenomena may affect the dispersal of the reaction-product contaminants. In particular, fissuring and roof collapse, which result from cavity formation, can destroy the integrity of the underground "reaction vessel" and permit the escape of pollutants to the surface or into overlying aquifers. Large areal gasification operations could also lead to significant surface subsidence, with results that may be important environmentally, and in their effects on process facilities.

WATER SAMPLING AT HOE CREEK I

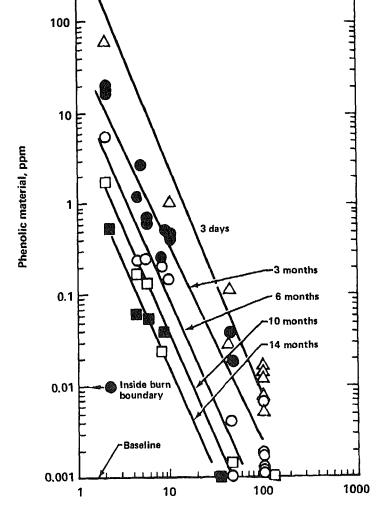
Measurements of changes in ground-water quality near <u>in situ</u> coal gasification experiments are of importance, initially, in that they help to define the contaminant source. That is, they permit a description of the composition, concentration, and early-time distribution of the underground contaminants. Such measurements also provide information concerning short-term changes in concentration and composition that are a result of chemical reactions, sorption by coal and other media, or biological action. Over a period of several years, the water quality measurements will begin to yield information concerning the possible development of a plume of contaminated ground water that may spread outward from the gasification site in the direction of natural ground-water flow.

We have carried out extensive ground-water quality investigations at the sites of both LLL <u>in situ</u> coal gasification experiments. Approximately a dozen wells in the vicinity of the first gasification experiment (Hoe Creek I) were monitored before, during, and after gasification ^{4,5} The samples were analyzed in the field and, much more extensively, at the laboratories of the U. S. Geological Survey, the Research Triangle Institute, and LLL. A simplified summary of the data is given in Table I.

		Inside burn zone			outside burn zone	
Species	Pre-gasification value (mg/1)	Concentration (mg/1)	on Increas	se	Concentrati (mg/1	
Phenols	0.001	0.1	100 >	x	500	5 x 10 ⁵ x
CN ⁻	0.01	0.4	40 >	x	300	$3 \times 10^4 \times$
NH ₄ +	0.5	20	40 >	x	70	100 x
DOC	6	4	-		200	40 x
Br ⁻	0.1	1.0	10 >	×	4	40 x
Pb ⁺²	0.001	0.001	40		0.04	40 x
Ba ⁺²	0.1	-	-		1.0	10 x
K ⁺	5	60	10 >	×	45	8 x
Li ⁺¹	0.03	0.3	10 >	×	0.2	6 x
Mg ⁺²	10	50	5 >	ĸ	60	6 x
S0√2	200	2000	10 >	ĸ	1000	5 x
Ca ⁺²	40	600	20 >	ĸ	200	5 x
B (III)	0.1	0.7	7 x	‹	0.5	5 x

Among the chemical species that show a large increase as a result of the gasification experiment are the phenolic materials, which represent the largest group of organic contaminants introduced into the underground environment by this experiment. The changes in concentration of the phenolic materials, as a function of time and distance from the boundary of the gasified zone, are shown in Fig. 2. Notice that the phenol concentrations have decreased by roughly two orders of magnitude at all distances from the burn zone. Although most other contaminants are also decreasing⁵, their rates of decrease are not, in general, as rapid as those indicated in Fig. 2.

The water from selected wells was analyzed by the Research Triangle Institute using a method that combines gas chromotography and mass spectrometry (GC-mass spec). This technique (now also employed at LLL) provides detailed information concerning volatile and semi-volatile organic contaminants. The coal gasification process produces an enormous variety of such organic by-products. The more volatile aromatic materials such as benzene, toluene, xylenes, and napthalene penetrate into the porous media surrounding the gasification zone. As illustrated in Fig. 3, the species of lower molecular weight (more volatile) are transported further from the gasification zone. A discussion of some limitations that apply to quantitative comparisons of the GC-mass spec data with results obtained by other methods will be found in Ref. 5.



Distance from burn boundary, ft

Figure 2. Concentrations of phenolic materials as a function of distance from the nearest burn boundary of the Hoe Creek I in situ coal gasification experiment. Times are measured from the end of gasification. Sampling wells are completed in the gasified coal seam and located in various directions from the gasification zone.

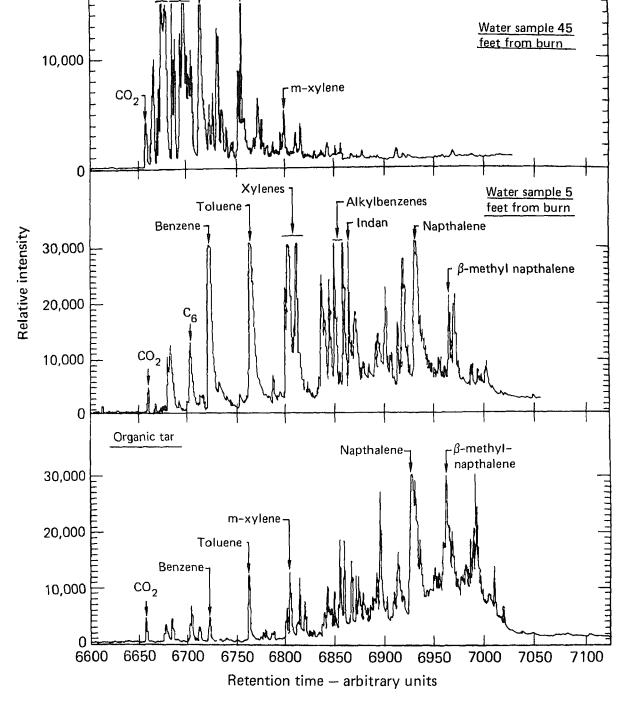


Figure 3. Chromatograms of volatile organics found in product tar and in water obtained 5 ft and 45 ft from the burn zone. The numbers on the abscissa are related to the chromatograph retention times.

Note that the lower-molecular-weight (more volatile) species move much further out into the formation, and that the organics in the nearby water are more like the product stream tar.

provide evidence concerning changes in contaminant concentrations that may occur as a result of natural ground-water flow. In principal, phenol concentrations in the outer wells might ultimately increase. Nevertheless, the rapid and uniform decrease in the concentrations of phenolic materials over a period of more than a year is an encouraging example of the self-cleansing capabilities of coal aquifers.

LABORATORY AND COMPUTATIONAL STUDIES

A clearer and more quantitative understanding of the ground-water changes near an underground gasification operation can be achieved by means of laboratory investigations carried out in conjunction with the field measurements. Of particular interest, are the nature and magnitude of the cleansing actions that occur when contaminated water is exposed to coal. Results such as those shown in Fig. 4 leave little doubt that phenol is rapidly adsorbed by coal. More elaborate experiments involving the flow of contaminants through a column of coal (Fig. 5) are also underway. They establish values of the distribution coefficient, $K_{\mbox{\scriptsize d}}$, which is a measure of the fractional adsorption of a dissolved contaminant and an essential ingredient in contaminant transport modeling. Our modeling efforts include the development of a 2-dimensional computer code capable of predicting transient dispersion of contaminants introduced continuously from a line source. The model includes convection, longitudinal and lateral dispersion, and adsorption. 6

GROUND-WATER EFFECTS AT HOE CREEK II

Nine ground-water sampling wells were provided for measuring ground-water quality changes resulting from the second Hoe Creek experiment. Since the second experiment involved the gasification of 20 times as much coal as Hoe Creek I, it would be of considerable interest to compare ground-water changes near the two sites. Such a comparison might help to establish the dependence of the contaminant source strength on the amount of coal gasified. In particular, the comparison might indicate whether the concentrated "shell" of phenolic materials just outside the burn zone is a surface effect or dependent on the entire gasified volume. Unfortunately, a straightforward and meaningful comparison of ground-water measurements at the two sites is impossible, for reasons discussed below.

We have sampled the ground-water near the Hoe Creek II site before, during, and several times after gasification. Some analyses are performed in the field, and preserved samples are sent for extensive analysis to U.S. Geological Survey laboratories, Gulf South Research Institute, and LLL. The

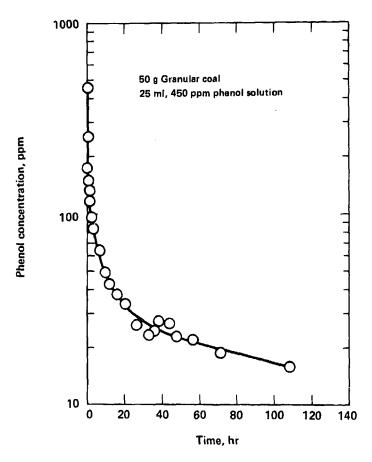


Figure 4. Laboratory measurements of phenol adsorbed by granular coal as a function of time. The data represent the analysis of a large number of equivalent phenol solutions agitated with a shaker table.

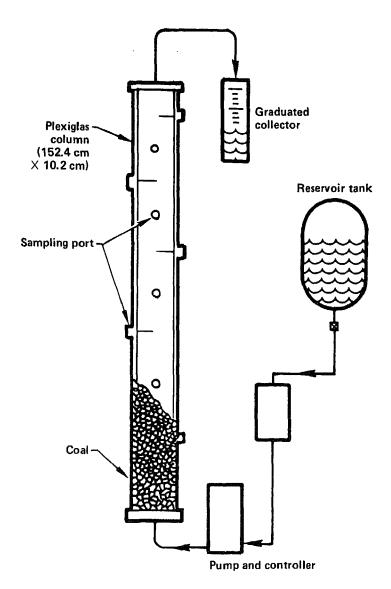


Figure 5. Coal column apparatus used to simulate the flow of contaminated ground water through a coal seam.

During operation, samples are extracted through rubber septa using a hypodermic syringe.

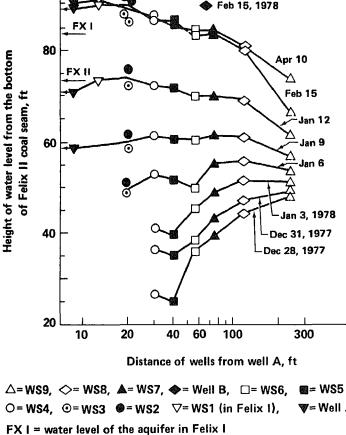
concentrations are expected to depend very strongly on well locations relative to the burn boundary (Fig. 2), and this effect could account for large differences in measured concentrations. However, a more important difference stands in the way of a simple comparison of contaminant levels near the two sites. Water level data (Fig. 6), subsurface geotechnical measurements, and post-burn coring investigations show that cavity roof collapse connected the gasification cavity with overlying aquifers (The Felix I Coal and a coarse channel sand above it). Since the Hoe Creek site is a recharge area (hydraulic head decreasing with depth), water from the overlying aquifers is flowing into the gasification cavity and producing an abnormally high hydraulic head within the cavity. Calculations based on the data of Fig. 6 suggest that ground-water flow rates in the immediate vicinity of the cavity exceed normal flow rates by at least an order of magnitude. Preliminary data on phenol concentrations (Fig. 7) showed a temporary increase in concentration in some of the sampling wells, which are completed in the Felix II Coal. Evidently, source concentrations and source geometry were significantly affected by the aquifer interconnection. The environmental implications of the altered contaminant distribution are being investigated.

Another question whose importance is emphasized by the aquifer interconnection at the Hoe Creek II site concerns the possibility that contaminants from the gasification zone may migrate into overlying aquifers. Additional sampling wells recently completed in the Felix I aquifer will help to answer this question. It may be that the downward flow of water in a recharge area will minimize the spread of contaminants into overlying aquifers. In any case, the importance of an enlightened choice of site selection criteria is becoming increasingly apparent.

SUBSIDENCE STUDIES

Since ground deformations induced by the gasification cavity may play an important role in determining contaminant dispersal and may, in addition, lead to significant surface subsidence, an improved understanding of these subsidence phenomena is of outstanding importance. We are attempting to extend out knowledge of these effects and develop a reliable predictive capability through a combination of laboratory tests of overburden cores, geotechnical measurements at the site of ongoing gasification experiments, and finite element modeling.

A preliminary modeling study of the subsidence induced by underground coal gasification was conducted in preparation for the first Hoe Creek experiment. In the treatment employed, a stratified overburden is stressed by gravity loading and by the removal of coal seam elements in a manner simulating coal combustion. The resulting stresses, strains, and displacements are determined for the duration of the excavation process and for subsequent quiescent periods during which plastic deformation and stress relaxation gradually take place in the rock and soil strata. Inelastic



FXII = water level of the aquifer in Felix II

Water levels in wells near the Hoe Creek II in situ Figure 6. coal gasification experiment. The water levels are plotted as a function of distance from the injection well "A" at various times following gasification. (A logarithmic distance scale is used to avoid data crowding for the close-in wells.) All wells are completed in the gasified Felix II coal seam except WS-1, which was completed in the overlying Felix I coal aquifer. The data show how water levels have changed since air injection was terminated at the conclusion of the gasification experiment on December 25, 1977. The elevated water levels in the vicinity of the gasification zone suggest that the gasification cavity has been interconnected with the overlying Felix I coal aquifer, which lies about 20 feet above the Felix II Coal, and with another aquifer above the Felix I Coal.

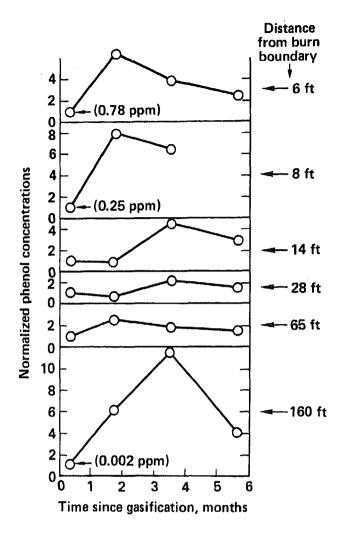


Figure 7. Changes in the measured concentrations of phenolic materials in the Felix II coal aquifer as a function of time after gasification. The measurements were made in some of the wells shown in Figure 5. These and other data suggest that the contaminants are moving outward away from the gasification zone. This movement appears to be much exaggerated in the immediate vicinity of the gasification zone as a result of an interconnection with an overlying aquifer. (Note that the actual magnitudes of the phenol concentrations measured in the close-in wells are hundreds of times greater than those in the outermost well.)

subsidence was detected.

An augmented version of the above method was used in an effort to predict subsidence and ground movement for the Hoe Creek II experiment. Two sets of assumed values of material properties were employed, termed "probable" and "lower bound". We also added a new feature to our method of modeling the excavation process associated with gasification. As the computations proceeded, roof material that developed tensile stress was mathematically removed in a subsequent iteration. In other words: as coal elements were "gasified" and zones of tensile stress appeared in the roof, those zones were "spalled" or allowed to collapse. This procedure produces a shallow arched roof, free of tensile stress, such as might be expected to occur naturally.

This augmented model also predicted surface subsidence of only an inch or so. On the other hand, relatively large deformations, and considerable roof caving were predicted below the surface. It seemed clear that subsurface measurements would produce the most helpful data - both for understanding the implications of subsidence for the <u>in situ</u> gasification process, and as a guide in checking and improving our subsidence modeling capabilities. Subsequent measurements have shown that a combination of roof caving and combustion (in the overlying Felix I Coal) caused portions of the cavity to be extended some 70 ft above the top of the Felix II Coal, much higher than predicted.

In an effort to provide subsurface data, we designed an array of geotechnical instruments for installation in the overburden at the site of the Hoe Creek II experiment (Fig. 8). The instruments included two 6-position borehole extensometers (Fig. 9), two electrical shear strips, a multiple piezometer installation, and a borehole deflectometer apparatus that was utilized in six specially cased boreholes. Provisions for surface measurements included specially designed isolation bench marks, an optical level, and a precision tape extensometer. A detailed description of these instruments, their deployment at the Hoe Creek II site, and some preliminary results are reported by Ganow et al. in reference 9. An analysis of the geotechnical data (obtained before, during, and after the Hoe Creek II experiment) has provided a relatively clear picture of the overburden deformation and roof collapse that occurred in response to the growth of the gasification cavity. Of particular interest, is the fact that the extensometers and piezometers documented the interconnection of the gasified coal seam with the overlying Felix I and channel sand aquifers.

Since a variety of measurements have shown that roof collapse extended significantly higher than predicted, we are attempting to develop modeling methods that take account of process-related phenomena that may be significant. Roof spalling due to shrinkage effects induced by heating may be an important factor in determining the utlimate cavity size. A preliminary attempt to incorporate these shrinkage effects into the calculations is described by Greenlaw et al. in reference 10.

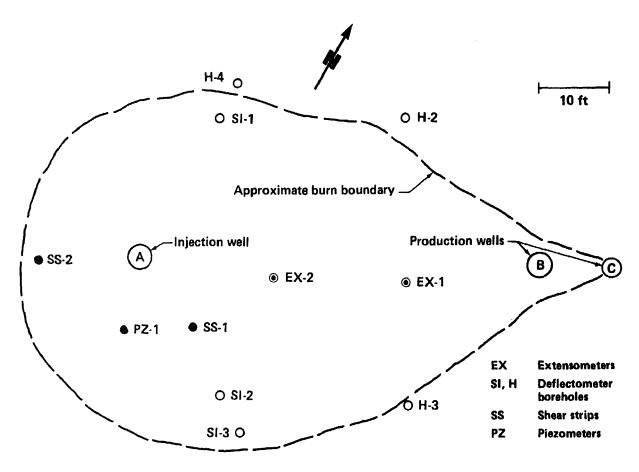


Figure 8. Plan view showing process wells and subsidence instrumentation boreholes at Site II.

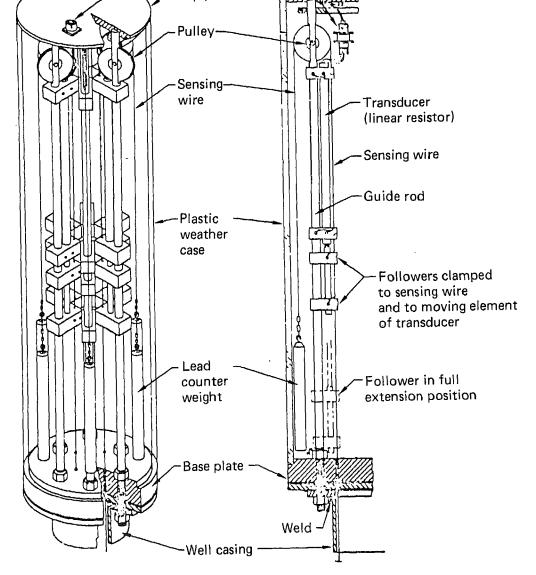


Figure 9. Multiple-position borehole extensometer sensing head. Cables from the sensing head extend down to expandable mechanical anchors located at various positions in the overburden. Displacements measured at the sensing head are the integrals of vertical strains occurring between the head and the various anchor points.

The usefulness of 3-dimensional solutions will also be explored. We are hopeful that an improved knowledge of subsidence behavior in actual gasification experiments, used in conjunction with properly measured overburden characteristics, can permit the development of predictive modeling capabilities that will be a reliable guide to the subsidence phenomena that may accompany large scale in situ coal gasification.

ACKNOWLEDGMENTS

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INTRODUCTION

High temperature entrained flow coal gasifiers have a well-known advantage over lower temperature fixed-bed or stirred-bed gasifiers. This advantage is the marked reduction in tars, phenols, and other condensible hydrocarbons as gasifier by-products. For example, Lurgi fixed-bed gasifiers produce from 50-100 pounds of tar, 30-70 pounds of tar oil and naptha, and 8-12 pounds of phenols per ton of coal (1,2). Similar by-product compounds and yields have been reported for a fluidized bed gasifier operated by the Pittsburgh Energy Research Center (3). On the other hand, the Koppers-Totzek and Texaco High temperature entrained flow gasifiers are claimed to produce negligible amounts of tars and oils as by-products. The gas and water purification equipment is, therefore, less complicated and less expensive than that required for the Lurgi process. It was anticipated that more advanced high temperature entrained flow gasifiers would also have this advantage.

The experimental gasifier studied in this report is housed at the Eyring Research Institute in Provo, Utah. This gasifier is a pressurized, entrained-flow gasifier that has a capacity of ~50 pounds of coal per hour and has a downflow configuration with some similarity to an entrained flow gasifier operated by the Bureau of Mines during the period 1952-1963. It also has some similarity to the Texaco entrained flow gasifier configuration.

2. PROCEDURE

A diagram of the laboratory gasifier and the necessary coal feeding, gas cooling and cleaning, and ash handling equipment is shown in Figure 1. Pulverized coal from a pressurized feed hopper is fed to the gasifier entrained in a stream of recycle gas. The coal is rapidly mixed and reacted with a mixture of super-heated steam and oxygen. The reaction is carried out at pressures of 75 to 150 psig and gasifier outlet temperatures of 2300-2800°F. Residence times for gasification reactions are of the order of 0.1 second.

The gasifier products pass downward into a quench section where they are

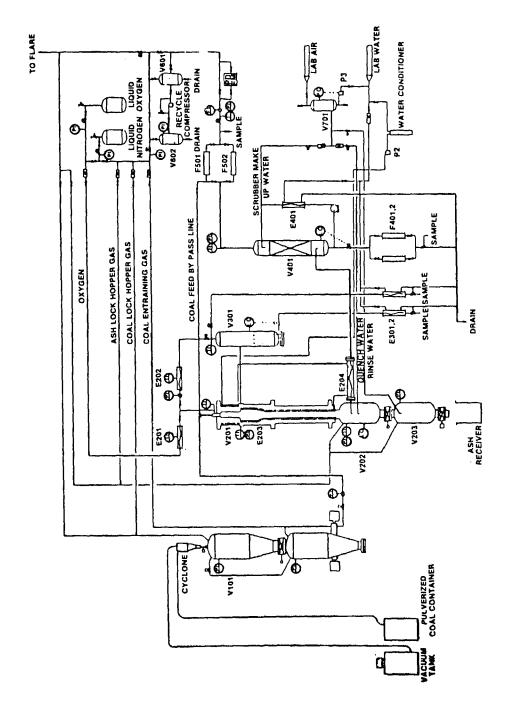


Fig. 1. Flow Diagram of Laboratory Scale Gasifier

		-
V101	Coal lock vessel	18" × 57"
V102	Coal feed vessel	18" × 57"
V201	Gasifier section	10" × 12"
V202	Ash/slag accumulator vessel	10" × 4"
V203	Ash/slag lock hopper	10" × 3'
V301	Steam drum	$4" \times 4"$, 18 kw heater
V401	Scrubber column	10" × 4"
V601	Recycle gas inlet vessel	12" × 6'
V602	Recycle gas accumulator	14" × 6'
V701	H.P. water accumulator	10"! × 3"
E201	Oxygen heater	3/8" × 40' coil, 5 kw
E202	Steam superheater	3/8" × 40' coil, 5 kw
E203	Steam evaporator	3/8" coil
E204	Economizer exchanger	19 tubes, 3/8" × 2'
E301,2	Condensors	5" × 24"
E401	Scrubber water cooler	60,000 BTUH
	Garathan 14 man 5416 an	·
F401,2	Scrubber liquor filter	8" × 34", 4.4 sq. ft.
F501,2	Product gas filter	4" × 24"

In this study, a detailed characterization of products and by-products associated with this gasifier was performed. Four process parameters, as shown in Table 1, were varied; coal feed rate, reactor pressure, oxygen to coal ratio, and steam to coal ratio. A high-volatile, non-caking, Utah bituminous coal was used for most of this study. A simplified flow chart showing the gasifier effluent streams is shown in Figure 2. Samples were taken from the cooled and water-scrubbed product gas stream, the scrubber effluent water, and the gas evolved on depressurization of the scrubber water. The gas samples were analyzed by gas chromatography and selective reaction indicator cartridges while the scrubber water was subjected to the analysis scheme shown in Figure 3. The scrubber water was first filtered to remove the particulate matter. Portions were then analyzed by proton induced x-rayemission (PIXE) and atomic absorption spectroscopy, thermometric titrimetry, and ion chromatography. Both the filtered scrubber water and the particulate matter were extracted with methylene chloride and analyzed by gas chromatographic mass spectrometry.

Table 1
Gasifier Test Parameters

Reactor Pressure (psia)	75	150	
Coal Feed Rate (lbs./hr.)	20	40	60
Oxygen to Coal Ratio (wt/wt)	0.8	0.9	1.0
Steam to Coal Ratio (wt/wt)	0.1	0.3	0.5

RESULTS

Analysis of effluent streams at median gasifier conditions. The data in Tables 2 through 5 represent the average of three gasifier test runs that were made under identical reactor conditions: coal feed rate = 40 lbs. of Utah bituminous coal/hour, reactor pressure = 150 psia, oxygen to coal ratio = 0.9, and steam to coal ratio = 0.3. Table 2 shows the product gas composition. Gases which were specifically tested for and not found at the sensitivity level of 0.5 ppm include SO_2 , COS, NH_3 and CS_2 . The composition of the flash gas obtained during depressurization of the scrubber is given in Table 3. Again, SO_2 , COS, NH_3 , and CS_2 were not detected.

Table 4 shows the net elemental composition of the scrubber water after subtraction of concentration levels measured in the water before scrubbing. PIXE analysis can detect nearly any element between atomic numbers 14 and 40 above an approximate detection limit of 0.5 ppm. The detection limits for heavier elements are somewhat higher. Notice that the data are given both in units of ppm in scrubber water and lbs per ton of coal feed. It was found impossible to compare our data with data from other gasifiers because of the inavailability of certain gasifier operating parameters.

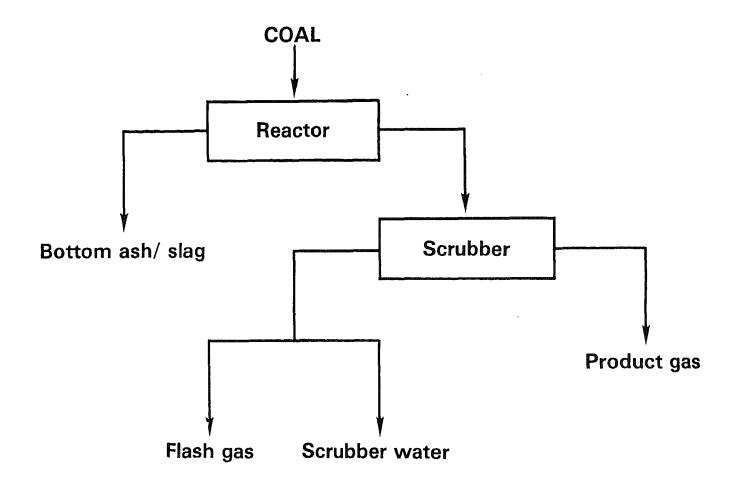


Fig. 2. Gasifier Product and Effluent Streams

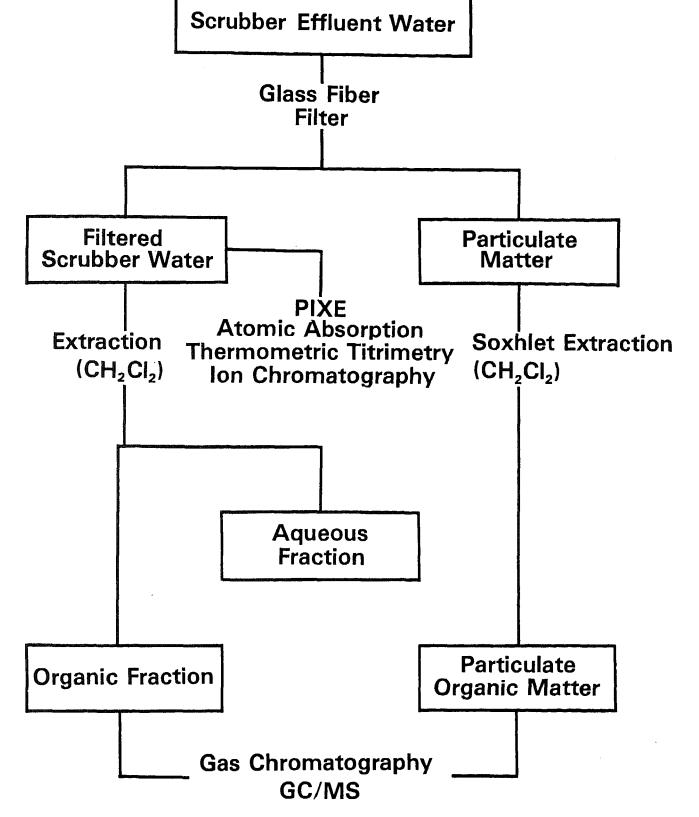


Fig. 3. Flow Diagram of Scrubber Water Analysis Procedure

CO	54%	2300	co ₂	31%	14.0
H_2	30%	88	N ₂	34%	9.9
co ₂	11%	690	cō	31%	8.9
N_2^{2}	5%	200	CH ₄	0.4%	0.6
cH ₄	0.7%	15	H ₂ S	0.4%	0.14
H ₂ s	550 ppm	3	H ₂	4%	0.007
HCN	1 ppm	0.004	HČN	44 ppm	0.001

Table 4

Filtered Scrubber Water Elemental Composition

Flement	ppm	1bs/ton of Coal
Ca	50	4.6
S	8	0.78
Si	3	0.28
Fe	2	0.22
C1	3	0.30
Zn	1	0.13
K	1	0.09
Sr	0.3	0.03

Table 5

Filtered Scrubber Water Inorganic Species

Species	ppm	lbs/ton of Coal
HCO3 ⁻	210	19.0
C1-	9	0.85
F-	1	0.11
NH4 ⁺	45	4.12
NO ₃ -	0.6	0.03

The reporting of data in terms of weight per weight or weight per volume of pollutant in scrubber water is important from an environmental standpoint, but nearly useless for quantitative gasifier production comparisons because of the variability in scrubber water flow rates. In fact, an effluent stream can appear to be quite clean when data is presented in terms of ppm, when in reality the seemingly low levels of pollutants are a direct result of a very fast scrubber water flow rate. For this reason, we report quantitative data both in

Cu, Ti, Mn, Ni, Br, Hg, Se, and As detected at same level both before and after scrubbing.

Other elements (14 \leq Z \leq 40) not detected (<0.5 ppm).

 $S0_4^{2-}$ and $S0_3^{2-}$ detected at same level both before and after scrubbing.

Carboxylic acids, phenols, and amines not detected (<5 ppm).

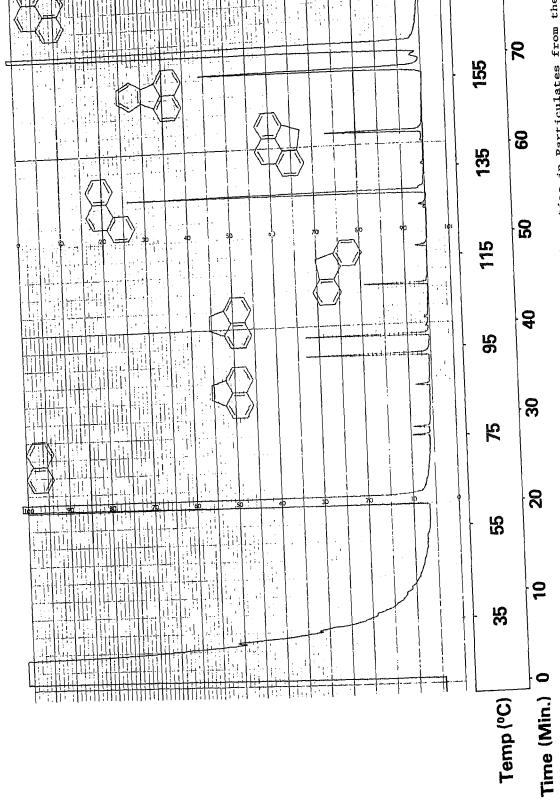
ion chromatography and thermometric titrimetry. Species not detected and approximate sensitivity levels are shown.

An interesting aspect of this study was the analysis of the organic compounds present in the scrubber water. After filtering 1.5 liters of the scrubber water through a 1.2μ pore filter, extracting 2 times with 100 ml each of methylene chloride, evaporating almost to dryness, and injecting the total amount into a gas chromatograph, essentially no organic compounds were found. On the other hand, the methylene chloride extract of the particulate matter which was filtered from the scrubber water contained significant amounts of organic compounds, all of which are polycyclic aromatic hydrocarbons. Figure 4 shows a capillary column gas chromatogram of the organic extract of the particulate matter of one sample. All peaks represent fused-ring aromatic systems. The absence of alkylated compounds is expected from a high temperature system.

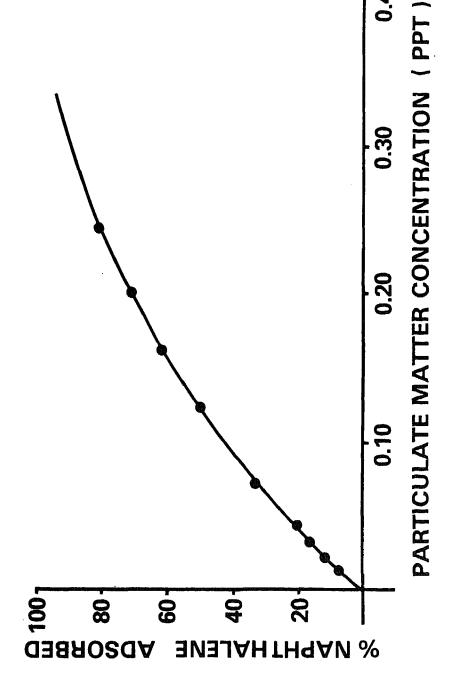
There is only approximately 1×10^{-3} lbs. of extractable organic material in the unfiltered scrubber water per ton of coal consumed, and the total amount is quantitatively adsorbed on the particulate matter. Natusch (4) has recently presented a theoretical model describing the quantitative adsorption of polycyclic aromatic hydrocarbons onto fly ash due to the sudden decrease in temperature as the fly ash exits from the stack of a coal-fired power plant. It appears that the same process is occuring as the product gas stream is cooled by the spray of water in the scrubber column. We tested the adsorption of naphthalene on particulate matter in water by dissolving 15 mg of naphthalene in one liter of distilled water which was thermostated at 22°C and successively adding portions of previously extracted particulate matter. After each addition, the amount of naphthalene adsorbed was determined by UV absorption. Figure 5 shows the adsorption curve obtained. Notice that 100% adsorption will be obtained at approximately 0.40 ppt particulate matter in the water. Scrubber water from the gasifier typically contained about 2% particulate matter so there is clearly sufficient to adsorb all of the organics from the water.

From the data in Tables 2-5 it may be concluded that (1) the effluent streams from this type of gasifier are extremely clean when compared to other types of gasifiers, (2) all of the nonvolatile organic compounds produced are quantitatively adsorbed by the particulate matter in the scrubber water, and (3) the only potential pollutants from the gasifier other than the soot in the scrubber water and the bottom ash/slag are the H₂S and HCN in the product and flash gases and NH₄+ in the scrubber water. The HCN is present in such small amounts that it probably is not environmentally significant.

Effects of gasifier conditions on effluent streams. Table 6 summarizes the significant effects of changing the gasifier operating conditions. Decreasing the pressure in the gasifier from 150 psia to 75 psia decreased the CO output per ton of coal by a factor of about 1.5. This is a large loss of coal conversion efficiency. The output of HCN, polycyclic aromatic hydrocarbons as represented by naphthalene, and scrubber collected soot all increased.



GC Separation and MS Identification of Polyclclic Aromatics in Particulates from the Fig. 4.



Adsorption Isotherm for Naphthalene on Particulate Matter from the Scrubber Fig. 5.

	Pressure 150 75 psia	Coal Feed Rate 60 → 40 → 20 1bs/hr	1.0-0.9-0.8 1b/1b	0.5+0.3+0.1 1b/1b
		Product Gas		
CO	decrease x 1.5ª	No effect then decrease x 1.8ª	С	С
H ₂	С	c .	С	С
CH ₄	increase x 2 ^b	decinc. x 4 ^b	increase x 4ª	С
H ₂ S	С	С	decrease x 4ª	С
HCN	increase x 6 ^b	c	С	С
		Flash Gas		
CO	c	c :	С	С
H ₂	С	increase x 7 ^b	С	С
H ₂ S	C	С	С	С
HCN	increase x 3 ^b	С	С	С
		Scrubber Water		L
NH ₄ +	С	increase x 2 ^b	С	decrease x 2 ^b
Total on soo	naphthalene t increase x 7ª	decrease x 3 ^b	С	С
Soot	increase x 4 ^a	decrease x 5 ^b	С	С

a. Most significant changes.

These results suggest that operating at pressures higher than 150 psia may result in better coal conversion efficiency and lower outputs of these pollutants. Attempts to run at higher pressures in the present gasifier resulted in mechanical problems, however.

Decreasing the coal feed rate below 40 lbs/hour also caused a large decrease in CO production. In this case production of naphthalene and soot were decreased.

Decreasing the $O_2/coal$ ratio in the reactor produced the only significant decrease in H_2S found. Changing the $O_2/coal$ ratio from 1 (wt/wt) to 0.8 re-

b. Not significant in comparison to other changes.

c. No effect.

In conclusion, higher pressures and lower O2/coal ratios should be studied to see if the trends observed in this study continue to change with the gasifier parameters.

Sulfur chemistry. The whole question of the reactions of sulfur in the gasifier is an important area for further research. About 25% of the sulfur in the coal ends up as H₂S in the product and flash gases, another 10% ends up dissolved in the scrubber water as ionic species, and the remaining two-thirds of the sulfur is present in the bottom ash/slag and scrubber collected soot. The chemical state and fraction of the sulfur in the bottom ash/slag is unknown at present. The particulate sulfur collected in the scrubber is elemental sulfur which is tightly bound in the soot matrix. Sulfur was removed from the soot at a constant rate by Soxhlet extraction of the soot with CH₂Cl₂ for several days. Such extractions never appeared to be complete.

The elemental sulfur in the soot is probably formed by oxidation of H_2S by oxygen containing groups on the surface of the graphitic soot particles. Similar behavior of activated charcoal which has been exposed to oxygen has been observed in other studies. The presence of peroxides in the scrubber water was also inferred from the results of thermometric titrations of acidified scrubber water with $Cr_2O_7^{2-}$. An understanding of these reactions could lead to new methods for scrubbing H_2S from gas streams.

The soot produced in this gasifier and collected in the scrubber water thus serves two beneficial functions: (1) the quantitative removal of polycyclic aromatic hydrocarbons from the water and (2) the partial removal of H_2S from the product gas.

Gasification of other carbonaceous fuels. Preliminary experiments on other types of coal, lignite, and COED char indicate that gasifier conditions can be adjusted to gasify these fuels as cleanly as the bituminous coal.

5. CONCLUSION

If economical and simple means can be found to remove the residual H₂S from the product and flash gases and the soot from the scrubber water, this type of gasifier has the potential of supplying clean gas from coal with very little environmental impact on water on air quality.

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ACKNOWLEDGEMENT ,

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INTRODUCTION

Increasing demands for natural gas and oil, partly caused by needs for environmental protection, have led to the inevitable situation where demand exceeds the U.S. productive capacity. The trade deficit from importing these clean fuels plus the uncertain political situation in the Middle East have prompted a drive for energy self-reliance in the United States.

Coal is a dirty, cumbersome fuel whose use in the past has been extensive, often with unfavorable consequences to the environment. Nevertheless, coal constitutes over 70% of the total estimated ultimately recoverable fossil fuel resources in the U.S. and will obviously be important in meeting future energy demands.

Besides being directly fired in boilers for generating steam to drive turbines and provide process heat, coal may be used for producing chemicals and clean fuels. Coal is used throughout the world as a raw material for synthesis of fertilizers and chemicals. This production generally uses a gasification system, such as Lurgi, Koppers-Totzek, or Winkler, to generate synthesis gas (usually hydrogen or a mixture of hydrogen and carbon monoxide).

Koppers-Totzek technology has had commercial application in atleast 12 countries since 1955. The Texaco gasification process, which has been tested with coal at the semi-commercial scale and has operated commercially with oil in over 20 countries since the 1940's, is planned for commercial application in combined cycle power plants. ¹

Potential emissions from entrained flow coal gasifiers, such as the K-T and Texaco, are presented in this paper. Commercial control systems for treatment of potential emissions are discussed relative to their applicability to entrained flow gasifiers.

DESCRIPTION OF GASIFICATION TECHNOLOGIES

Commercial, or near commercial, coal gasifiers that employ an entrained flow contacting method include the Koppers-Totzek (K-T) gasifier, the pressurized K-T, and the Texaco gasifier. Description of these gasifiers are presented in the following discussion.

years to produce liquid fuels from coal.

The first commercial plant employing Koppers-Totzek gasification was completed in Finland in 1952.² Since that time, plants have been built in Spain, Japan, Belgium, Portugal, Greece, United Arab Republic, Thailand, East Germany, Turkey, Zambia, and South Africa.^{2,3} Plants at other locations are currently under construction.

The K-T process employs the partial oxidation of pulverized coal in suspension with oxygen and steam. The Koppers-Totzek gasifier, shown schematically in Figure 1, is a refractory-lined steel shell cooled with a steam jacket to produce low-pressure process steam. Coal, oxygen and steam are fed to the gasifier through opposing special metering heads or nozzles. Coal is pulverized to 70% through a 200 mesh screen and dried to from 2 to 8% moisture. Exothermic reactions create temperatures of 3300-3500°F at the gasifier outlet. About 50% of the ash is entrained with unburned carbon in the fuel gas while 50% flows down the refractory walls into a water quench at the base of the gasifier. Less than 2% of the coal carbon accompanies the ash streams. Flux is sometimes added to the coal to adjust ash fusion properties, such that the slag flows freely from the gasifier and does not solidify on the refractory wall.^{2,3}

Two-headed K-T gasifiers with opposing nozzles 180° apart are capable of gasifying about 400 tons/day of coal to produce 15,000 scfm of gas. The capacity is essentially doubled in four-headed units with two sets of opposing nozzles 90° apart. The larger two-headed units are 10 to 12 ft in diameter, tapering to 6 to 8 ft at either end; overall vessel length is 25 ft. with an inner volume of about 1000 ft³. Four-headed gasifiers have similar dimensions and double the inner volume.^{2,3}

Operational experience has shown that the gasification reactions can be controlled by monitoring the $\rm CO_2$ concentration in the product gas. The $\rm CO_2$ level indicates the extent of chemical reaction, and controls are adjusted to maintain the $\rm CO_2$ concentration within a preselected range. Typical results using a K-T gasifier are given in Table 1.

The flow diagram depicted in Figure 2 shows schematically equipment used for synthesis gas production. The fire-tube boiler is inclined from the exit of the radiant boiler to a venturi scrubber. High-pressure steam (up to 1500 psig) is generated in the boiler. The gas from the boiler passes to a two-stage venturi scrubbing system where the particulate level is reduced to 0.002 to 0.005 grains/scf. Large particles (95% of total) are removed in the first fixed venturi. A second adjustable venturi scrubber removes 99% of the remaining particles. After particulate removal, the gas is cooled to about 95°F with water in a packed tower. As in early designs, the gas is then compressed for sulfur removal.

Cooling and scrub water are recycled in a circuit shown schematically in Figure 2. Slag quench water is cooled to prevent evaporation losses, and makeup for water lost with the slag is provided from the cooling and scrub water circuit. Makeup water for the system is added to the packed cooling tower.

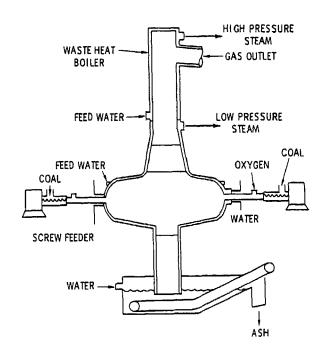


FIGURE 1. Koppers-Totzek Gasifier Schematic

TYPE OF FUEL	COAL	COAL	COKE
GASIFIER FEED Dry Feed to Gasifier Analysis, Wt% C H N S O Ash Moisture	72.7 5.3 1.1 1.0 9.0 8.9 2.0 100.00	69.9 4.9 1.3 1.1 7.1 13.7 2.0	88.0 4.5 1.4 4.3 1.0 0.2 0.6 100.00
Gross Heating Value of Dry Feed, Btu/Lb	13,135		15,690
Oxygen, Tons/Ton Dried Feed @ 98% Purity	0.878	0.849	0.950
Process Steam, Lb/Ton Dried Feed	814	810	1182
GASIFIER PRODUCTS Jacket Steam, Lb/Ton Dried Feed	600	554	629
High Pressure Steam, Lb/Ton Dried Feed @ 900°F/900 psig	2760	2675	3598
Raw Gas Analysis, Vol%, Dry CO CO ₂ H ₂ N ₂ + Argon H ₂ S COS	52.55 10.00 36.09 1.00 0.34 0.02	52.51 10.00 35.96 1.15 0.36 0.02	52.22 10.00 35.40 1.10 1.20 0.08
Dry Gas Make - SCF/Ton Dried Feed	100.00 69,690	100.00 66,970	100.00 77,500
Gas Gross Heating Value, Btu/SCF, Dry	287	286	283
<pre>% Heating Value of Gas/Heating Value Feed (Gross Basis)</pre>	76.1	75.8	69.9

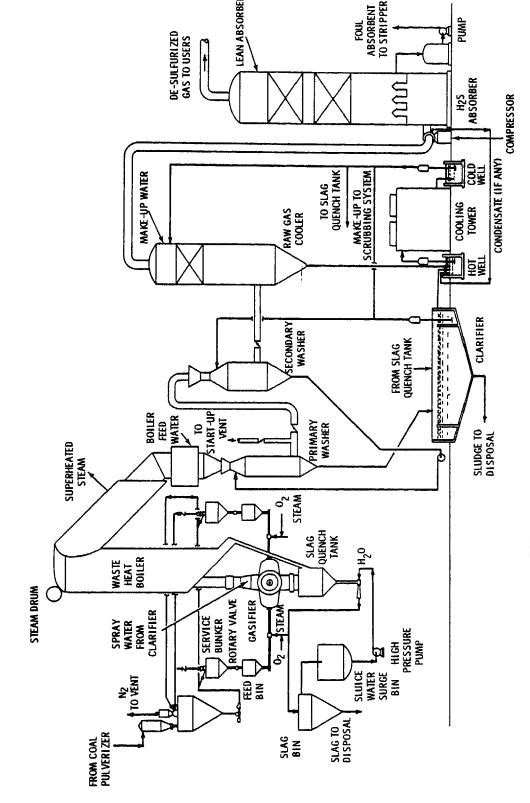


FIGURE 2. K-T Gasification Process Schematic

feed nozzles are arranged to inject the coal at velocities in excess of the flame propagation speed. The coal ash is completely liquefied in the flame zone, and about half of the ash in most coals drains from the bottom of the gasifier as molten slag into a quench tank. The remainder of the ash, which is entrained in the raw gas output, is generally solidified at the entry to the waste heat boiler beyond the gasifier by water spray injection to avoid ash adherence and build-up on the boiler surfaces. 4

Problems have been encountered in some recent installations of atmospheric pressure Koppers-Totzek gasifiers due to the very low viscosity of the slag from certain feed coals at the 2200 K (3500°F) burner tip temperature. The Koppers-Totzek design depends on build-up slag on the ceramic lining of the reactors to protect the linings. Not only did such build-up not occur, due presumably to the very low viscosity of the slag, but there was apparently reaction and/or solution of the ceramic lining with the slag, resulting in rapid failure of the linings. Moreover, whereas about half of the slag from the lignite feeds (which are common to most of the sixteen Koppers-Totzek plants now operating around the world) would normally be expected to flow out of the bottom of the gasifier directly into an ash quencher, it was found that no more than about 5 to 10 percent of the slag could be recovered in this way. Most of the slag was going over into the waste heat boiler along with the gas, greatly overloading the ability of the design to handle the solidifying mixture."

A partial solution to both of these problems has been to reduce the operating temperatures by increasing the steam-to oxygen ratio in the gasifiers. However, this has also decreased the carbon conversion efficiency

to "somewhat below 90 percent."4

Koppers (U.S.A.) indicates that they have developed designs for pressurized gasifiers operating at 60 psi and at 1000 psi and are seeking an underwriter for the construction of one or both of these systems. Presumably, only very small-scale reactors have actually been operated at these pressures. The primary stumbling block to pressurized operation has been the development of reliable coal feed devices.

Koppers (U.S.A.)⁴ has reported that Shell (Dutch) and Koppers (Germany) have operated a 5 t/d pilot unit near Amsterdam for over two years. The plant has operated successfully on all ranks of coals at a pressure of 450 psi, producing a gas whose composition consisted of about

95 volume percent CO plus H2, 2.6% CO2 and 0.3% CH4.

A 150 t/d unit constructed in Hamburg combines the experience of Koppers in the entrained bed gasification of solids at atmospheric pressure with Shell's experience on high pressure partial oxidation of liquids. The plant, which is highly proprietary, is expected to start operation by September 1978. Koppers (U.S.A.) is not involved in the development of the process, but expects to be able to license the process. They expect no commercial conclusion to be drawn with regards to the process before 1983

a) Information received by telephone from Mr. James W. Bumbaugh, Koppers, Engineering and Construction Div., Koppers Company, Inc., Pittsburgh, PA, August 1978.

TEXACO COAL GASIFIER

The Texaco gasifier was developed by Texaco, Inc. at their Montebello Research Laboratory in California during the 1940's. It was routinely operated from 1946 through 1954 to provide synthesis gas for an on-site pilot plant that was a modification of the Fischer-Tropsch process. Since 1953, the Texaco process has been in commercial use for the production of synthesis gas from petroleum feedstocks and is currently used in approximately 70 plants in over 20 countries. The process, which was initially developed for the partial oxidation of natural gas, has developed the versatility to use light oils, residual oil, petroleum distillates, asphalt, heavy oils, or coal as feedstocks. The Texaco process is the only high pressure suspension gasification process that has been operated on an industrial scale. Most of this experience has been with heavy oil as feedstock and dates back to 1953.

The Texaco gasifier is a vertical cylindrical pressure vessel (up to 85 atm) with a carbon-steel shell, the top section where gasification occurs is refractory lined. The lower section (slag quench chamber), which contains a reservoir of water for the quenching of gas, is unlined steel.⁶

Process flow diagram of the Texaco coal gasification pilot plant is shown in Figure 3. In the process coal, which has been ground to pass through a 40-mesh screen, is mixed with water in a slurry mix tank. The resultant slurry containing about 40 to 60 wt.% coal is pumped through an optional preheater to a temperature of 700-1000°F or more. The coal particle size has been reported to be reduced further in this heating coil, either as a result of attrition or as a result of the rapid expansion of water undergoing evaporation. Since the proportion of water required to slurry and pump the coal was greater than that required for efficient gasification, up to 75 percent of the steam is separated in a cyclone in front of the gasifier.

The coal feed slurry enters the reactor either axially at the top or tangentially near the top through a water-cooled burner nozzle of proprietary design. Preheated oxygen is fed through a separate water-cooled nozzle oriented to prevent impingement of oxygen on the wall of the reactor.⁸ Slag flows through a constricted opening at the bottom of the reactor into a quench tank and becomes granulated. The granulated slag. which is heavier than water and which generally contains less than one percent carbon by weight, is removed periodically from the bottom of the quench chamber by a lockhopper system. The fine solids, or soot, which are lighter than slag and which are principally ungasified carbon, are continuously removed from the quench section as an aqueous slurry. These solids are concentrated in a settling system and may be returned to the slurry preparation system if desired. Since the settling system operates at near-atmospheric pressure, flash gases are evolved with pressure letdown. The gases are reportedly very similar in composition to the product gas, except for a higher percentage of CO2 and H2S.5 If the clarified water from the settling system is recycled to the quench chamber and scrubbing section, a blowdown stream is required to maintain the total dissolved solids at a desired level.⁵ This stream reportedly contains no tars or phenols. The quenched product gas can be treated in an acid gas removal system.

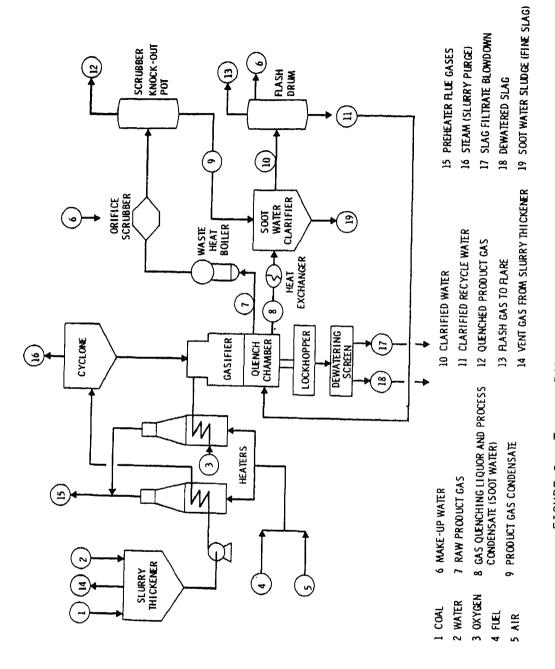


FIGURE 3. Texaco Pilot Plant Process Flow Diagram

plant so that its performance can be studied.9

The pilot Texaco gasifier at Montebello operates at pressures up to 350 psig and has a reaction volume of about two cubic feet. The temperature in the reaction zone ranges from 2000 to 2500°F. Throughputs of 1000 lb/hr of coal have been reported. Carbon conversions are primarily controlled by the amount of oxidant fed to the system, and are typically above 90 percent on a single pass basis. Only limited performance data have been reported¹⁰ with carbon conversions between 90 to 98%, thermal efficiency ranging from 75 to 80% and oxygen requirements of 350 to 375 scf/Mcf of make gas. The gas contained about 8% CO_2 , 1% CH_4 , and had a H_2/CO ratio of about one. It has also been reported that, the oxygen consumption rates ultimately expected are 15,000 to 20,000 scf per ton of dry coal with 80 to 90% of the heating value of the coal appearing in the form of hydrogen and carbon monoxide in the synthesis gas.

Very limited operating details and results using coal have been published for the Texaco process. Table 2 lists some typical results for gas, fuel oil, and coal firing.⁵ It should be noted that at least for fuel oil operations the distribution of sulfur compounds in the product gas was very similar to that calculated for equilibrium. As an example, Texaco cited a study in which the observed sulfur distribution as hydrogen sulfide, carbonyl sulfide, and carbon disulfide was 89, 11, and 0.03 percent, respectively; and the calculated equilibrium distribution was 93, 7, and 0.05 percent, respectively. 11

COMMERCIAL CONTROL SYSTEMS

The gasification of coal in an entrained flow system involves a number of processing steps. The steps in the direct process include coal storage, coal preparation, gasification, gas quenching, particulate removal and acid-gas removal. End use of the gas will determine if further gas processing, such as shift conversion, is required. In addition to the steps in the direct process, auxiliary facilities are required and usually include an oxygen plant, a sulfur plant, a utility boiler, raw water and waste water treatment facilities, and cooling towers.

The complexity of the multi-step process for coal gasification increases the difficulty of controlling environmental pollutants. All aspects of the conversion process, from coal storage to final product, require extensive study to assess the potential for pollutant emissions, determine actual emissions, and proceed to a control strategy which is technically and

economically effective.

Figure 4 presents a simplified schematic of the overall process and delineates possible effluents from each processing step, excluding the mining operation. Each operation involved in the conversion process, from coal storage through final gas utilization, is a potential source of environmental pollution. Effluents from auxiliary facilities should also be considered.

The following discussion relates to the operations that are somewhat unique to an entrained flow gasification process. Operations such as coal storage, coal preparation, oxygen production, and the utility boiler are

Fuel Type Fuel Composition, Wt.%	Natural Gas	Fuel 0il	Pittsburgh Coal	Japanese <u>Coal</u>
C	74.42	85.59	77.3	64.3
Н	21.94	11.38	5.3	4.9
0	1.67	0.35	5.2	15.0
N	1.98	0.72	1.4	0.9
S	-	1.96	2.5	1.8
Ash	•	-	7.1	13.1
Moisture	-	-	1.2	-
Fuel Rate, lb/hr	1714	429	-	-
Oxygen/Fuel, lb/lb	1.30	1.02	0.84	0.66
Steam/Fuel, lb/lb	-	0.38	0.70	0.67
Gas Composition, Mole % (dry)				
CO	38.02	47.97	46.6	45.7
co ₂	2.19	3.65	11.5	13.2
H ₂	59.54	47.45	38.7	37.9
CH ₄	-	0.44	0.7	0.6
N ₂	0.15	0.22	2.0	1.7
អ_s	-	0.02	-	-
cos	-	0.02	-	-
Gas Yield, scf(dry)/lb fuel	58.38	50.36	38.31	31.06
Materials per 1000 scf (CO + H_2)				
Fuel, 1b	17.6	20.8	30.6	38.5
Oxygen, scf	271.7	252.3	306	302
Steam, 1b	-	7.9	21.5	25.8
Carbon Conversion, %	100	96.6*	92.1*	91.3*

^{*}Calculated from reported data

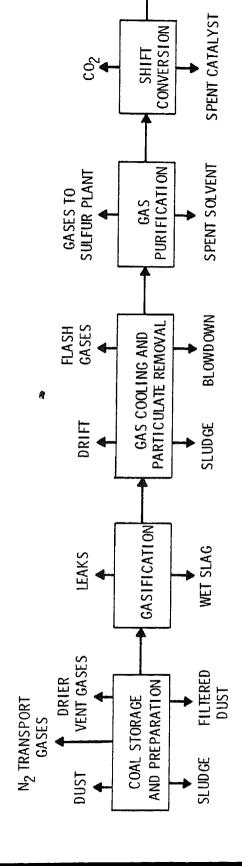


FIGURE 4. Effluent Streams From Coal Gasification

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pressurized K-1 and lexaco yasiliers.

GASIFIER OPERATIONS AND PARTICULATE REMOVAL

The objective of gasifier operations for the K-T and Texaco processes is to react coal with oxygen and steam to produce a synthesis gas consisting of H_2 and CO accompanied by varying amounts of CH_4 . During gasification other gases are produced, including CO_2 , N_2 , H_2S , COS, and C_2H_6 . Of these gases the sulfur compounds are of major consequence. Other potential pollutants may also be generated: tars, oils, phenols, ammonia, particulates, other organic material, and trace elements.

Although gaseous pollutants are produced in the gasifier, these are not of immediate environmental concern as they are contained in the raw gas leaving the gasifier and are treated in subsequent process treatment steps. Exceptions are emissions due to leaks in gasifier seals and in pressurized lock hoppers and other feeding systems. These leaks would allow gaseous pollutants to escape directly into the atmosphere and would be significant sources of pollution. This situation would require immediate correction.

Contaminated water streams appear to be the major potential source of pollution from the gasifier, gas cooling, and particulate removal systems. Solid residues in the form of ash, slag, soot and sludge will require land disposal. These solid residues will contain inorganic ashes, metals, and unreacted carbonaceous matter of unknown composition that may prove to be of consequence. At present most gasification schemes use mine backfill or landfill as the method of disposal for this material. This method of disposal may prove to be environmentally unsatisfactory for some wastes, especially ash residues that have a high potential for leachability. This problem can only be evaluated after complete analysis of specific gasifier waste streams.

Reaction zone temperatures in entrained flow gasifiers are necessarily high to achieve adequate conversion with a short residence time. Temperatures are in the range of 3300 to 3500°F in the K-T gasifier and 2000 to 2500°F in the Texaco gasifier. The product gas, therefore, contains no condensible hydrocarbons. No phenols, pyridines, or organics are produced. However, ammonia and cyanide are present in the K-T product gas. Gas analyses before and after particulate removal for a K-T system are shown in Table 3. 12 The analyses shown in Table 3 represent operating data from a plant using a primary and secondary venturi scrubber in which the gas is intimately contacted with recirculated water.

Discharges to Air

In the atmospheric pressure K-T system, discharges to the air could result from stripping the components dissolved in scrub water and direct contact cooling water by air in the cooling tower (see Figure 2). No further discharges to the air environment are foreseen since the product gas from particulate removal is compressed and passed to the acid gas removal system for further processing.

As shown in Table 3, some components are retained in the scrub water and cooling water. 12 All concentrations after particulate removal should increase by a factor of 1.3 over concentrations before removal because of the decrease in H_2O concentration resulting from condensation. Components retained in the scrub water are COS, HCN, SO_2 and NO. These could be stripped by direct contact cooling of the scrub water.

Volume Percent

Component	Before Particulate Removal	After Particulate Removal
CO CO2 CH4 H2 N2 H2S COS HCN NH3 H2O Ar SO2 NO Particulates (grains/scf)	37.36 7.13 0.08 25.17 0.30 0.23 178 ppmv 288 ppmv 0.17 29.19 0.32 22 ppmv 7 ppmv 11.57	49.50 9.42 0.11 33.35 0.40 0.3 15 ppmv 300 ppmv 0.22 6.20 0.42 15 ppmv 7 ppmv 0.002

In the Texaco system, possible contamination of the air environment could result from combustion of gases from the flash drum, see Figure 3. These gases are flashed from scrub water and quench water solutions after pressure letdown in the flash drum. These gases will probably have a composition similar to the product gas but richer in components such as CO2, H2S, COS, SO2 and NO. This stream may require treatment before it can be flared.

Discharges to Water

In commercial K-T plants, the reduction in particulate concentration shown in Table 3 is accomplished in the washer cooler, venturi scrubbers and separator. About 50% of the ash content in the coal leaves the gasifier as a slag quenched in water at the base of the gasifier.

Water flow in the cooling and scrubbing system proposed for U.S. applications is shown in Figure 2. Solids retained in the water are removed in a clarifier. If water is not a premium consideration, a slurry can be pumped to a disposal area. Water conservation can be effected by filtering the slurry, returning the water to the circulating system, and disposing the filter cake by truck or railroad car transfer to the worked-out mine or disposal area. Since all the particulate matter is slagged in the gasification process, leachable contamination should be low. Water loss with the ash may serve as blowdown for the cooling towers.

Analyses of water from the various cleaning and cooling stages in the Kutahya, Turkey, plant are shown in Table 4.¹² This table shows the level of water contamination that occurs in commercial practice. Not all trace element concentrations are noted in Table 4; proposed drinking water

standards, EPA 1975 limits, are 0.2 mg/l for cyanide.

Process Water Analyses from Koppers-Totzek Gasification TABLE 4.

				Sam	ole Location		
Property		-	2	3	4	2	9
Hd		8.8	8.8	8.9	7.5	8.8	8.8
Conductivity	S	7.6×10^{-4}	1.8x10 ⁻³	2.0×10^{-3}	9.7×10 ⁻⁴	1.8×10 ⁻³	1.8×10 ⁻³
Ca0	mq/g	78	101	78	85	135	179
MgO	mg/k	97	191	194	102	145	113
Na Na	mg/ &	17.5	17.5	17.5	17.5	17.5	17.5
×	mq/ g	5.6	8.8	10	8.9	8.0	8.0
Zn	mg/k	0.01	0.03	0.02	0.03	0.02	0.02
Fe	mq/g	0.05	0.22	1.95	0.26	0.20	0.64
NH,	3 / Su	0.32	157	184	25	137	122
N05	3 / bm	0.02	0.13	4.47	5.34	0.24	4.37
NO,	mg/ g	58.2	3.32	13.7	34.0	24.7	22.9
PO ₄ Total	mg/ &	1.89	0.81	1.21	1.69	0.81	2.70
. [3	mg/g	18	85	96	53	22	46
S04	mg/g	42	216	155	147	255	109
CN	mg/ &	0.26	0.52	12.5	7.0	1.4	14.0
H2S	mg/ &			W	ot detected		
KMn04	mg/ &	œ	თ	400	74	_	145
Consumed							•
000	mg 02/ ℓ	14	18	128	18	91	63
SiO2	mg∕ g	14.8	16.0	14.8	30.6	19.8	42.6
Suspended Solids	mg/&	14	4612	5184	278	3072	50
Cu	უ/ გ	0.01	0.01	0.01	90.0	0.01	0.00
	{						

Cooling water to gasifier seal pot.
 Water from gasifier seal pot.
 Wash water after washer-cooler.
 Wash water after Theisen washer.
 Water into clarifier.
 Water out of clarifier.
 Water out of cooling tower.

loss from the scrubber cooling tower (16,220 lb/hr drift loss with coal feed rate of 562,500 lb/hr, 8,830 BTU/lb, from Reference 14) with the composition shown in Column 7 of Table 4 are included in Column 3 of Table 5 for comparison of releases to the standards even though drift losses are not a direct water discharge. Releases from drift loss approach the standards and indicate that water releases must be minimized, or waste water must be treated prior to release

It may be necessary to steam strip gaseous components such as NH₃, SO₂, and HCN from the clarifier water before it passes to the cooling tower to prevent their being stripped by direct contact with air. Koppers proposes to remove a bleed stream from the recirculated water system to a steam stripper. Gaseous NH₃, SO₂, and HCN flow to a Claus unit and are combusted while the stripped water is cooled and returned to the circulating system.

Considerations for the pressurized K-T and Texaco systems are similar to those for the K-T system. Water for gas cooling and scrubbing can be treated and recycled. Water streams from the Texaco process that must be treated include water from the slag quench chamber in the lower half of the gasifier unit, gas quenching liquor and process condensate, and clarifier water.

TABLE 5. Adjusted New Source Performance Standards (pounds of pollutant per 10¹² BTU feedstock, 30 day maximum) (a)

<u>Pollutant</u>	Petroleum Refineries	Coke Making	K-T Drift Loss Estimate
BOD	230-1015	477	200 (COD)
TSS	143-646	242	190
Ammonia (as N)	46-400	242	180
Oil and Grease	71-233	12	•
Phenols	1.5-7.1	5.8	~
Sulfide	1.2-5.8		

⁽a) Assumes heating values of 6.5 mm BTU/bbl of crude oil and 12,000 BTU/lb of coal, with a coke yield of 0.69 lb coke/lb coal.

dissolved matter, is drawn off near the bottom of the quench chamber and sent to a clarifier. No quantitative information is available on the characteristics of this stream; however, it is expected that the water will contain components such as shown in Table 4. Scrubber water (process gas condensate) from the scrubber knock-out pot is also sent to the clarifier. This stream is expected to contain suspended coal fines and slag, CN, S=, ammonia, trace elements and organics. 15

Water from the clarifier in the Texaco System is circulated to the flash drum where flash gas is vented to a flare. Make-up water is added to the clarified water in the flash drum and the water is recycled to the

quench chamber.

Discharges to Land

Sludge from the clarifier and slag from the quench system for entrained flow gasifiers are usually sent to landfill. The sludge may be dewatered by filtration either before or after transport to a disposal site. Since all the solids have been slagged, very little leaching to ground water should result. The water associated with the slag and sludge will have the compositions shown in Table 4, columns 2 and 6 respectively.

Ash from the clarifier and slag quench system could have properties that significantly differ from power plant fly ash. 16, 17, 18, 19 Ash from gasification processes is exposed to a reducing atmosphere, and elements may exist in a reduced form. Trace metals may be more soluble than fly ash trace elements in a number of water streams. This is likely to change effluent loadings to the waste water treatment facilities and, therefore, require alternative water treatment techniques. Furthermore, a change in solubility may affect the leachability of inorganic compounds present in the final slag to be disposed and runoff from disposal areas will have to be monitored until firm data is established. Koppers-Totzek has reported data on major components in some of their water streams (see Table 4), but no data are available on trace elements. No information on trace elements is available on slag quench, sluice, or elutriation waters. From the water analyses in Table 4 it is apparent that the ash from Kutahya plant would render the soil basic. Unlike mine refuse and coal preparation refuse, the residue from gasification does not contain sulfur (pyrite) which causes the acid mine drainage problem.

Discharges to land from entrained flow gasifiers is predicted not to cause any environmental problems. Since the ash has been slagged, dust problems from disposal sites should be minimal. Disposal sites should be monitored to characterize runoff streams.

ACID GAS REMOVAL

The removal of contaminants, especially sulfur, is a critical part of the gasification of coal. Contaminants that could potentially be present in the impure gas from entrained flow gasifiers consist of sulfur in the form of H₂S, COS, SO₂, and organic sulfur compounds, as well as nitrogen oxides, ammonia, cyanides, pyridines, hydrocarbons, odors, trace elements (Pb, Se, As, Te, F, Hg, Ga, Ge, Cd) that volatilize at gasification temperatures, and particulates. Gases from entrained flow systems are usually very low in hydrocarbons because of high reaction zone temperatures.

of reducing sulfur content in the gas to 0.1 ppm to 5 ppm. Carbon dioxide is also selectively removed in these processes along with the sulfur gases.

Other processes have been proposed for the removal of acid gases. One of these is the Benfield Hot Carbonate Gas Purification process followed by sponge iron and activated carbon traps, as proposed for the Synthane process. Koppers-Totzek processes will use one of the three already mentioned processes, while proposed Lurgi gasification facilities will use the Rectisol process or the Stretford process for H2S removal.

Commercial processes for removal of sulfur gases are listed in Table $6.^{20,21}$ These processes are usually insensitive to pressure, high pressure operation being preferred. The efficiency of these processes for removal of H₂S is dependent on the concentration in the gas to be treated, but usually about 99% of the H₂S is removed. Regeneration of the solvent is accomplished thermally or with steam. In the chemical solvent and physical solvent processes, the H₂S stream from regeneration is usually sent to a Claus plant where it is converted to elemental sulfur. In the direct conversion and drybed processes, regeneration produces elemental sulfur directly.

Discharges to Air

Gas purification has several potential release areas. A scrubbing system that uses a solvent must periodically dispose of spent solvent or regenerate it in some manner; either alternative could cause environmental problems. The extent of this disposal problem is dependent on the lifetime of the solvent and characteristics of the contaminants. If the H₂S containing stream is not oxidized in a Claus plant, another problem may arise. This problem involves traces of other components, such as NH₃, COS, or light hydrocarbons, that may be present along with the H₂S. These compounds may go through the sulfur production step unaffected, or may interfere with the sulfur recovery process.

Discharges to Water

Removal systems can be designed to reduce liquid effluents to zero pollutants. Purge streams are usually incinerated to eliminate discharges to water. Alternatively, depleted solution may be sent to waste water treatment.

Discharges to Land

No solid effluent streams are encountered in acid gas removal. Elemental sulfur is produced in the Claus plant.

AUXILIARY FACILITIES

Facilities not directly in the process flow include the oxygen plant, sulfur plant, waste water treatment plant, makeup water treatment plant, the cooling tower, and the utility boiler. Some of these auxiliaries are needed to treat effluents from the main process.

The auxiliary facilities represent well-developed technologies that have been in commercial use for many years. In most cases, their application to entrained flow gasification processes, such as the Texaco and K-T, is not unique. Possible exceptions include the sulfur plant (Claus plant) and the waste water treatment plant.

•			
Process	Absorbent	Type of Absorbent	Temp. °F
Chemical Sol- vent type:			
MEA	Monoetha- nolamine	Aqueous solution	80 to 120
DEA	Dietha- nolamine	Aqueous solution	100 to 130
TEA	Trietha- nolamine	Aqueous solution	100 to 150
Alkazid	Potassium dimethyla- mino ace- tate	Aqueous solution	70 to 120
Benfield	Activated potassium carbonate solution	Aqueous solution	150 to 250
Catacarb	Activated potassium carbonate solution	Aqueous solution	150 to 250
Physical sol- vent type:			
Sulfinol	Sulfolane + Diiso- propanomine	Organic solvent	80 to 120
Selexol	Polyethy- lene glycol ether	Organic solvent	20 to 80
Rectiso1	Methanol	Organic solvent	<0
Direct Con- version:			
Stretford	Na ₂ CO ₃ + anthraqui- none sulfonic acid	Alkaline solution	
Drybed type:			
Iron Sponge	Hydrated Fe ₂ 0 ₂	Fixed bed	70 to

to process surpped gases with a high toy content relative to H25. Efficiency of sulfur recovery decreases as the inlet concentration of HoS to a Claus plant decreases. An inlet concentration of over 20 volume % ${
m H}_{2}^{2}{
m S}$ is desirable. The presence of ${
m CO}_{2}$ in high concentration can also present problems by reacting with H2S to form COS. With the availability of Claus tail gas cleaning processes, adequate commercial technology for sulfur control is available for use with entrained flow systems. Sulfur recovery in the form of sulfuric acid and elemental sulfur is being practiced at K-T installations throughout the world.

Applicable commercial processing steps for waste water treatment include stripping for removal of dissolved gases (H2S, NH3, CO2), clarification for removal of suspended solids, biological oxidation, and sand filtration. The main waste water sources are the slag quench water, particulate scrub water, and spent solvent solution. Waste waters from entrained flow systems will be low in dissolved organics since the high qasification temperatures destroy heavy organics. The low organic content

should simplify waste water treatment.

ENERGY REQUIREMENTS

The environmental impact of an operation can be related directly to the energy used for that operation. It is, therefore, extremely important to determine the areas in a system that require large amounts of energy.

Energy requirements for different operations employed in the K-T gasification process were determined from literature sources and are tabulated in Table 7. Sources of information are referenced in the table.

TABLE 7. Process Energy Requirements

Operation	Required Energy, % of Gasifier Input Koppers-Totzek
Coal Preparation (drying and grinding)	6.3 ^(a)
Particulate Removal	(<) (b)
Compression	15.4 ^(a) (7.2) ^(c) 4 - 7 ^(d)
Acid Gas Removal .	4 - 7 ^(d)
Oxygen Plant	11.1 ^(e) (16.9) ^(a)
Sulfur Plant	16)
Tail Gas Cleanup	0.1 ^(f)
Cooling Water Pumps, Air Fans	1.8 ^(a)

Data from Reference 14, calculated as described above. (a)

Data from Reference 22, pp. 20-100 to 20-108. (b)

Adiabatic compression to 165 psig. (c)

(d) Data from Reference 23.

Data from Reference 20, p. 14. (e)

(f) Data from Reference 24. pound of steam was considered to cost 1500 BTO of fossil energy and 10,000

BTU of fossil energy produced 1 kWh of electricity.

Generation of the oxygen required for coal gasification and gas compression are the major users of energy in the gasification systems. Coal preparation (mainly drying) and acid gas removal are also large users of energy. Examination of process improvements in these areas, therefore, have the greatest potential for energy savings. Decreasing energy demand will benefit the environment in direct proportion to energy savings. However, the areas represented as large energy users represent highly developed technology. It is unlikely, for example, that significant energy saving improvements in oxygen plant operation can be expected. Acid gas removal processes can be selected on the basis of their energy requirement, e.g. steam requirements for solvent regeneration vary significantly for different processes.²³

CONCLUSIONS

Several conclusions may be drawn from this study:

l. Coal storage, preparation and drying processes are commercially available. Coal storage and handling methods used by coal-fired power plants should be directly applicable to gasification using Koppers-Totzek and Texaco gasifiers. Crushing and drying requirements for gasification are somewhat more severe than those encountered by coal-fired power plants.

- 2. Sulfur and particulates are completely removed from the product gas in the commercial operations as required for use of the gas for chemical synthesis. These systems have been in use for over 40 years. Claus plants are employed in some of these commercial operations to convert the sulfur compounds to environmentally acceptable elemental sulfur. Reduced H₂S concentration in stripped gases to the Claus plant will reduce efficiency for sulfur recovery.
- 3. Tail-gas cleanup processes for reduction of Claus plant emissions and increasing sulfur recovery are available.
- 4. Major energy users in the processes are oxygen production, acid gas removal, and gas compression.
- 5. Since essentially no tars or hydrocarbons are produced in entrained flow gasification processes, water cleanup problems are minimal and should cause no unique waste water treatment problems for conventional water treatment methodologies. Dissolved compounds such as NH4, H2S and HCN and leached trace elements are the contaminants of concern. Waste water will be cleaned and recycled for process use. Chronic loss of water results from direct contact cooling tower operation. Control of losses from evaporative cooling towers is a major concern.
- 6. Large quantities of ash and slag will be generated with commercial gasification processes. An assessment of ash compositions and ash disposal techniques should be undertaken to determine the adequacy of current control methodologies.
- 7. Although much information has been written about coal gasification processes, there are many areas in which data is lacking in the environmental aspects of the processes. These areas include: 1) determination of the fate of trace metals, especially those considered to be volatile and hazardous, 2) quantification of volatile emissions from cooling towers,

from clarifiers and slag quench tanks, 6) determination of the chemical properties of clarifier effluent and sludge, and 7) a better general characterization of most process streams.

RECOMMENDATIONS

This study and previous studies reveal that, with the possible exception of trace elements, adequate control technology is commercially available. Improvements in these technologies are needed to reduce energy requirements and environmental releases. The major need is to demonstrate that the control systems give adequate cleanup with actual process streams. This can be done in two ways:

1. Characterize flows and control equipment performance in existing operating plants.

2. Install production capacity based on the gasification technologies and thoroughly characterize flows and environmental releases at these installations.

The first option involves getting permission from operating plants to instrument their facility to determine process flows and to monitor the area surrounding the plant. EPRI funded a study on gasification of COED char in a K-T gasifier at Puentes, Spain. The report on the results of this study has not been issued at this time. The fact that COED char was gasified in a K-T unit at Puentes, Spain, indicates that cooperation with operating plants and foreign countries is possible. However, operators are usually very sensitive concerning studies relating to environmental releases, and the flexibility in modifying or changing processing conditions would be severely limited in testing at a commercial facility.

Installation of production capacity based on these gasification technologies is the recommended approach. Rather than install units in a highly industrialized area such as Cedar Bayou, Texas, as recently announced, 25 it is recommended that units be installed where effects of trace elements and other releases can be thoroughly characterized.

The following steps are recommended to demonstrate the adequacy of environmental control technology for gasification:

• Install a 300 t/d (or larger) ammonia fertilizer plant in a non-industrialized area.

• Thoroughly characterize the state of the environment at the plant location before operations begin.

 Monitor releases from the plant during operations. Determine all process flows in the operating plant.

• Determine trace element behavior to see if any mechanisms for accumulation of toxic quantities are acting.

Successful demonstration of the project in an industrially undeveloped area would answer questions of environmental concern. Results would be extremely valuable in establishing environmental standards. This would allow employment of a technology to use coal to produce a product that is presently a large consumer of dwindling supplies of natural gas.

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Coal conversion processes employing wet cleaning of gases transfer a major fraction of coal chlorides and fluorides to the gas condensate. The presence of halides and other strong electrolytes, absorbed from the gas or leached from particulates, compromises the prospects for reuse of the condensate.

Preliminary absorption of halides involves a controlled two stage quench that collects particulates and absorbs strong electrolytes in a segregated, low volume, primary condensate. The larger volume secondary condensate collected from the second stage quench is amenable to partial desalination by steam stripping of volatile weak electrolytes and biological treatment for removal of organic compounds.

A study was made to assess the technical and economic feasibility of two stage gas quenching at a hypothetical producer gas plant operating on alternate feeds of high halide Eastern coal and low halide Western coal. The results indicated that a first stage quench collecting 10 percent of the total condensate would absorb over 99 percent of gas chlorides and over 97 percent of gas fluorides. Some thiocyanate was presumed to collect in the secondary condensate that compromised the efficiency of weak electrolyte removal by steam stripping and biotreatment. The ratio of electrolyte concentration for treated primary condensate to treated secondary condensate for Eastern and Western coals was 89 to 1 and 18 to 1 respectively. Comparative cost estimates of two-stage quenching versus single stage quenching with desalination of effluent by reverse osmosis indicated that two-stage quenching was more economical for high halide Eastern coal and that reverse osmosis was more economical for low halide Western coal.

It was concluded that the two stage quench system was economically favored as compared to reverse osmosis desalination of single stage condensate where the gasifier gas contains high halide content and/or high moisture content. The two-stage concept is considered to be widely applicable to coal conversion processes employing wet gas cleaning.

The mechanism and location of thiocyanate formation in two-stage quenching was not defined in the study. If thiocyanate forms during the first stage quench it is purged with the high electrolyte discharge. If thiocyanate forms during the second stage quench it will add to the electrolyte content of the secondary condensate that is reused in the process. Research is indicated to resolve the thiocyanate question as well as to any special materials requirements for the first stage quench system.

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Coal conversion processes employing wet cleaning of gases transfer a major fraction of coal chlorides and fluorides to the wastewater discharge. The presence of halides and other strong electrolytes in wastewater compromises the prospects for reuse, unless resort is made to energy intensive desalination technology.

An alternate concept to desalination involves the application of a two-stage gas quench where the first stage preferentially absorbs strong electrolytes in a low volume flow and the second stage comprising most of the condensate is collected relatively free of strong electrolytes. Thus the preliminary absorption of halides and other strong electrolytes in a low-volume first stage quench produces a condensate from the second stage quench that is relatively free of strong electrolytes. The volatile weak electrolytes present in secondary condensates can be stripped from the water and the organic substances can be removed by bio-oxidation to yield an effluent that has a low dissolved solids content.

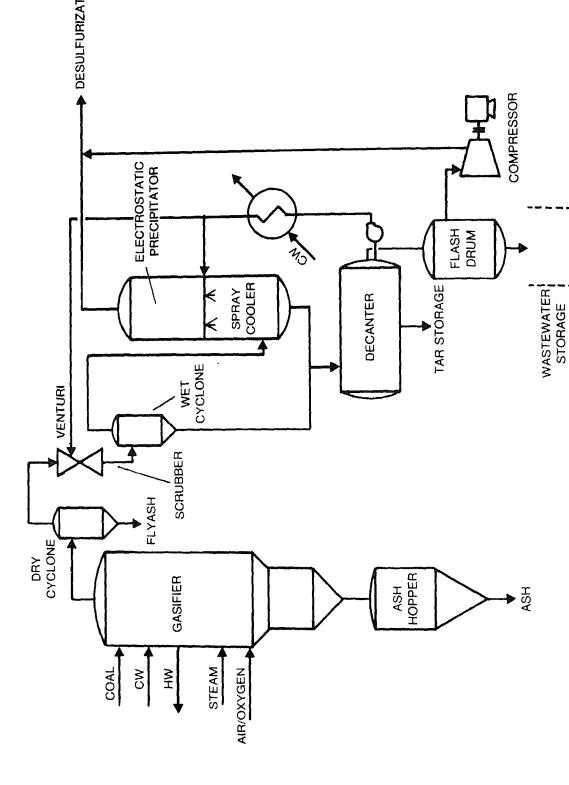
The purpose of the present study was the evaluation of the theoretical performance and economic feasibility of the two-stage gas quenching concept for a fixed bed coal gasification facility using 1500 tons per day of coal. The study compares the relative cost of two-stage quenching with single stage quenching plus equivalent desalination. The study examined both air blown and oxygen blown gasification technology, with air blown results selected for presentation herein. The analysis of performance is considered to be representative of tar producing coal gasification technology employing wet cleaning of producer gas. The analysis of practicality applies only to the system studied.

PROCESS DESCRIPTION

The hypothetical gasification plant selected for the study employed five 300 ton per day fixed bed gasifiers for an operational capacity of 1500 tons per day of coal. The gasifiers were modeled after the pressurized, stirred, fixed-bed gasifier of the Morgantown Energy Technology Center(1). The gasifiers had an assumed diameter of 13 feet and were operated air blown at a pressure of 103 psia. Steam at a pressure of 110 psig and a temperature of 350° F was injected into the gasifier and the outlet gas temperature was estimated as 1050° F. The gasifiers were operated on Illinois No. 6 coal and Montana Rosebud coal with analyses as reported in Table 1. The Illinois No. 6 coal was selected as representative of a high halide Eastern coal. The Montana Rosebud coal was selected as representative of a low halide Western coal.

The gas from the hypothetical gasifiers was passed through a dry cyclone and a heat recovery system to yield a feed to alternative gas cleaning systems at a temperature of 400° F and a pressure of 95 psia. The first system illustrated in Figure 1 provided conventional single stage gas cleaning consisting of a venturi scrubber, a spray cooler and an electrostatic precipitator to produce a cooled gas at 110° F. The second system illustrated in Figure 2 provided two-stage gas cleaning consisting of a venturi scrubber followed by a sieve tray absorber in the first stage and a spray cooler

	Ill. No. 6 Coal	Montana Rosebud <u>Coal</u>
	wt%	wt%
С	65.70	50.56
Н	4.80	3.18
S	3.70	1.09
N	1.10	0.90
0	8.04	9.81
C1	0.25	0.03
F	120ppmw	30ppmw
Ash	11.20	9.73
H ₂ 0	5.20	24.70
	100.00	100.00
Higher Heating Value, Btu/lb	11,750	8,611



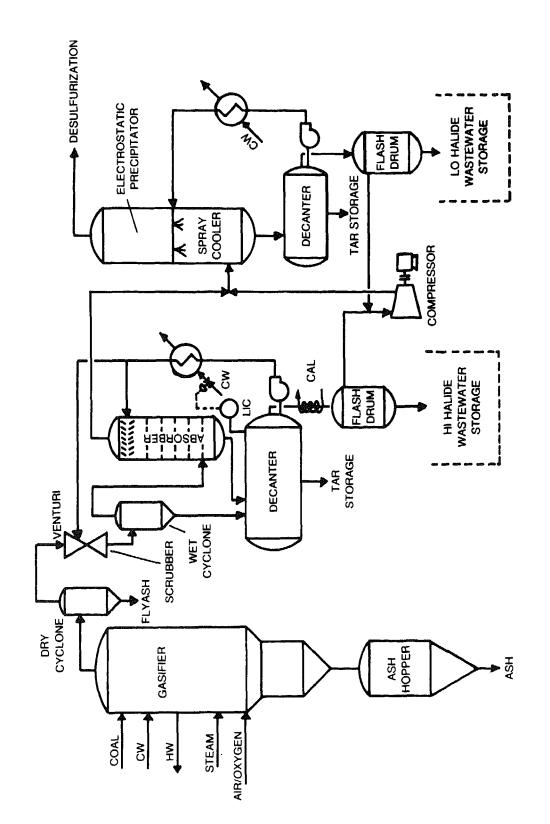


FIGURE 2: ILLUSTRATION OF GAS CLEANING BY TWO STAGE QUENCH

The second secon

E 1. 14: 000 5/

condensation was controlled by operation of the first stage decanter on a variable level basis in conjunction with a controlled blowdown from the system. The selected blowdown rate was proportioned to the air feed rate to the gasifier. The temperature of the quench liquid was controlled by the level in the decanter so as to condense more water as the level in the

decanter dropped.

Concepts for treatment of condensates collected from single stage and two-stage quenching are illustrated in Figures 3 and 4. The condensates discharged from the gasification process were stripped with steam for removal of NH3 and ${\rm H}_2{\rm S}$, which were returned to the gas prior to desulfurization. Separate strippers were required for first stage and for second stage condensates. Sodium hydroxide was added to strippers operating on single stage and first stage condensates to free fixed ammonia. The addition of sodium hydroxide was not required for the stripping of second stage condensates.

The bottoms from the strippers were biologically treated by the activated sludge process for removal of cyanides, thiocyanates, phenols and other organics. The effluent was filtered by granular media filtration for capture of fugitive suspended solids. Separate treatment facilities were required for condensates from first and second stage quenching.

METHODS

The study involved the conceptual design of process units, estimates of process performance and estimates of costs. The gas composition from the coal feeds given in Table I were estimated from material and energy balances keyed to operational data obtained from the MERC pilot plant stirred, fixed bed gasifier with heat losses taken as 2 percent of the total heat input. Where supplemental information was required for the analysis, performance projections were keyed to operating data from the Lurgi fixed bed gasifier at Westfield Scotland (2).

The chemical characteristics of the condensates were estimated with the assumption that equilibrium conditions were achieved in the absorption tower and in the spray cooler for the overhead temperature and pressure of each device. That is, the condensate blowdown was assumed to be in equilibrium with the vapor leaving the towers. Chemical equilibria were estimated by methodology of Edwards et. al. (3) supplemented by empirical correlations based on operational performance of similar systems.

The computer program (WAVES) developed in the reference predicts vapor liquid equilibirum for the system NH_3 - H_2S - HCN - SO_2 - H_2O . The program was modified to predict vapor liquid equilibrium for the system NH3 - CO2 -H₂S - HCN - HCl - HF - H₂O and applied to the prediction of condensate characteristics. The condensate characteristics predicted by the program were adjusted to include absorption of phenol, the presence of tar and the formation of thiocyanate. Thiocyanate formation is a complex phenomenon that was not resolved in the study. Based on coke plant correlations it was assumed that approximately 70 percent of the cyanide absorbed was converted to thiocyanate in the usual case where excess sulfur was present in the system.

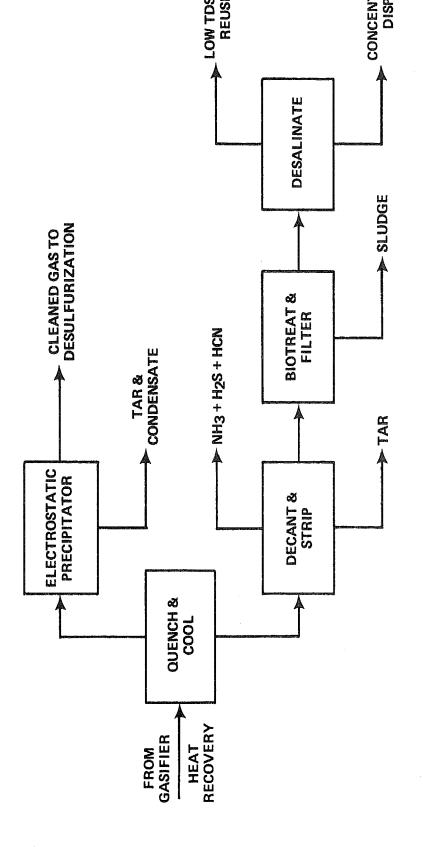


FIGURE 3: CONVENTIONAL GAS CLEANING AND CONDENSATE TREATMENT

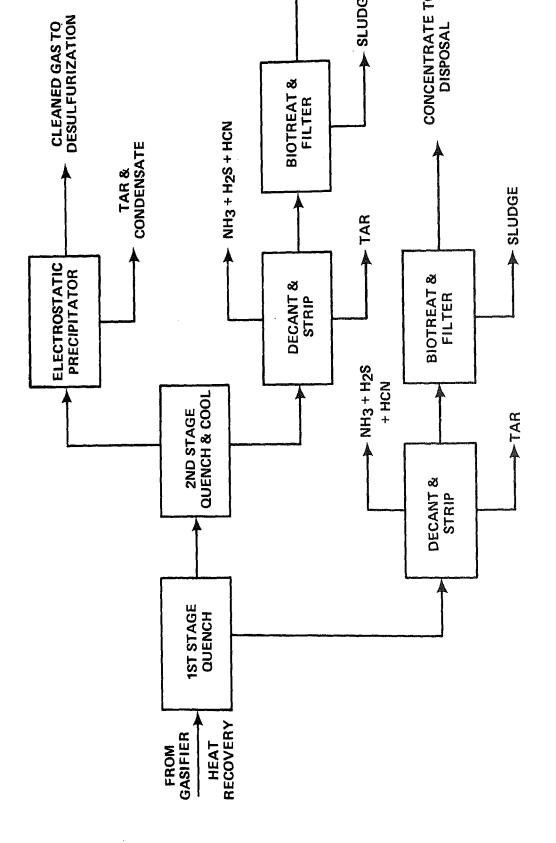


FIGURE 4: TWO STAGE GAS CLEANING AND CONDENSATE TREATMENT

Estimates of residual concentrations in the stripper bottoms were based on analysis of vapor-liquid equilibria adjusted by performance correlations from coke byproduct plants and petroleum refineries (4)(5). Based on performance correlations, the phenol residual in the stripper bottoms was estimated as 80 percent and total cyanide residual was estimated as 60 percent of input values.

The activated sludge facilities consisted of equalization, aeration, settling, granular media effluent filtration and attendant sludge dewatering systems. The systems were designed to operate in a temperature range of from 75 to 95° F at a sludge loading of 0.05 lbs. phenol per lb. mixed liquor volatile suspended solids. The performance of the systems was estimated from correlations with waste treatment results at coke plants and gasification plants.

Order of magnitude estimates were prepared to enable comparison of costs of conventional single stage quenching with costs of two-stage quenching. The estimates were prepared from engineering flow sketches and sized equipment lists. The scope of the estimates encompassed the gas cleaning trains, wastewater storage facilities, wastewater stripper facilities and wastewater treatment facilities. Order of magnitude estimates were also prepared for wastewater desalination by reverse osmosis.

RESULTS

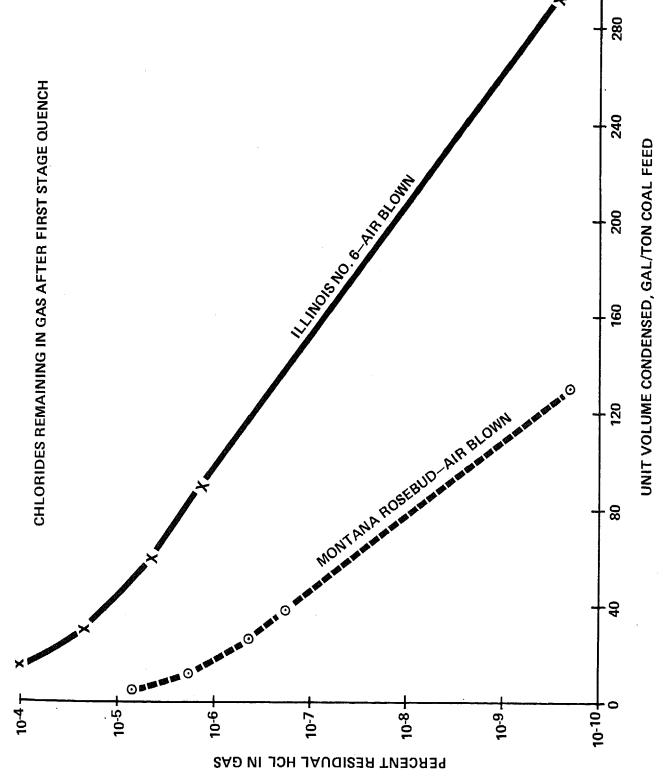
The higher halide and sulfur contents of the selected Illinois No. 6 coal described in Table 1 as compared to the selected Montana Rosebud coal yielded higher concentrations of HCl and HF in the gasifier raw gas as indicated in Table 2. Residual concentrations of HCl and HF in the cooled gas leaving the gas train were less than 0.0001 percent of gasifier gas concentrations. Thus halides were projected to be substantially removed by effective wet gas cleaning. For a given coal, the cooled gas leaving the electrostatic precipitator had essentially the same composition whether processed by single stage or two-stage quenching.

Figure 5 illustrates the predicted relationship for HCl absorption as a function of the water condensed in the first stage quench. The combination of the venturi scrubber (15 in wg. pressure drop) plus the sieve tray absorber with 9 trays was indicated to remove 99.9999 percent of the chlorides from Illinois No. 6 producer gas at a condensation level of 20 gallons per ton of coal fed. This constituted essentially complete removal of chlorides in the first 20 gallons (7 percent) of a total of 290 gallons of condensate produced per ton of coal fed. Somewhat higher absorption of HCl was projected for operation with Montana Rosebud due to increased alkalinity of the condensate.

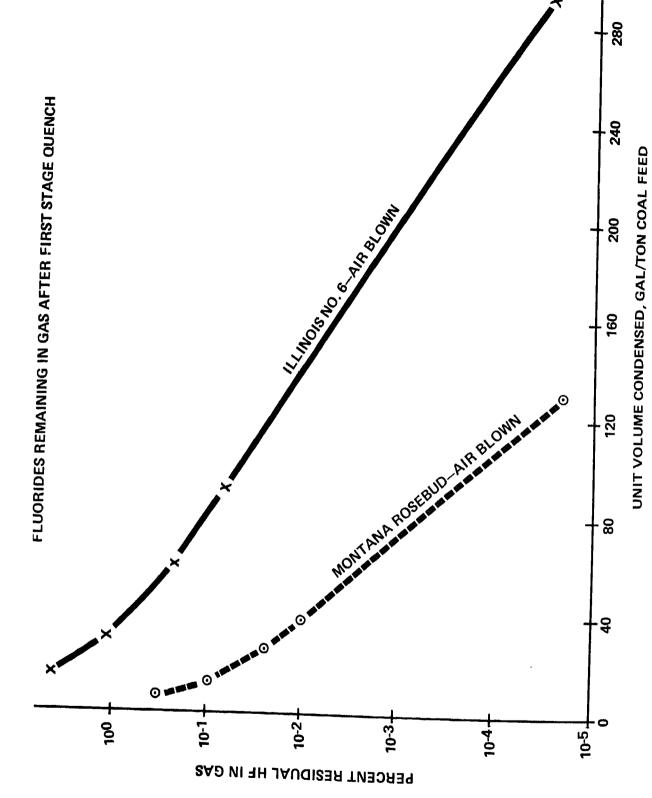
The predicted removal of HF as a function of volume of condensate is presented as Figure 6. With producer gas from Illinois No. 6 it was projected that a first stage quench of 30 gallons per ton would absorb over 98 percent of the HF from the gas. This amounted to 98 percent removal of fluoride in the first 10 percent of the total condensate. Fluoride removal from gas produced from Montana Rosebud was predicted to be higher because of increased alkalinity in the condensate. Thus the concept of preliminary absorption of halides was theoretically viable.

The projected results of steam stripping and biotreatment of condensates

	No. 6 Mole %	Montana Rosebud Mole %
CO ₂	9.56	11.72
CO	9.90	11.88
H ₂	15.01	16.32
H ₂ 0	30.73	21.23
CH ₄	1.59	1.69
C ₂ H ₆	0.14	0.17
H ₂ S + COS	0.47	0.22
N ₂ + A	32.38	36.47
NH3	0.17	0.27
HC1	311ppmv	60ppmv
HF	28ppmv	llppmv
HCN	173ppmv	272ppmv
	100.00	100.00
Higher Heating Value, Btu/scF	102.9	114.0
Gas outlet temperature ^o f	1050	1050
Operating Pressure Psia	103	103
Gas Flow SCFM	178,800	112,100



EFFECT OF UNIT VOLUME CONDENSED ON ABSORPTION OF CHLORIDES FIGURE 5:



EFFECT OF UNIT VOLUME CONDENSED ON ABSORPTION OF FLUORIDES FIGURE 6:

electrolytes such as NH3, CO2 and H2S. Free cyanide would also be quantitatively removed but it forms stable complexes of low volatility with metals such as iron and it reacts through various mechanisms with sulfur compounds during cooling of the gas to form thiocyanate - a strong electrolyte. Thiocyanate and metal cyanide complexes are refractory to the steam stripping process and therefore go with the stripper bottoms to biological treatment.

Biological treatment is projected to achieve excellent conversion of phenol plus substantial conversion of other organics and thiocyanates. The degradation of thiocyanate to ammonia and sulfate will contribute unwanted electrolyte to the second stage quench. The analysis projected that the strong electrolyte content of the second stage quench was 9 percent of a single quench and 1.1 percent of the first stage quench of 34 gallons per ton Illinois No. 6 coal feed. Thus the condensate from the second stage quench was of better quality for reuse than the condensate from the single quench.

The predicted results of steam stripping and biotreatment of condensates from gasifier operation on Montana Rosebud coal are presented in Table 4. The predictions forecast excellent removal of volatile weak electrolytes in the stripper and excellent removal of phenol by biological treatment. The strong electrolyte content of the second stage condensate was projected as 34 precent of the single quench condensate and 5.4 percent of the first stage condensate of 13.8 gallons per ton coal feed. The lower relative performance indicated for two-stage quench systems on Montana Rosebud was attributed to the lower halide content of the coal feed.

A cost comparison of single stage and two stage quench systems is facilitated by reference to Figures 3 and 4. The single stage quench will require a desalination operation to produce low electrolyte water for reuse whereas the two stage quench entailed the inclusion of a sieve tray absorber in the first stage quench and independent facilities for decanting, stripping and biotreatment of the first stage condensate.

Table 5 presents a comparison of estimated capital cost differences for the hypothetical gasifiers designed for air blown operation on Illinois No. 6 and Montana Rosebud coals. The capital cost for gas cleaning and condensate treatment systems was higher for two stage quenching than for single stage quenching. The difference was estimated as 2.2 million dollars for operation on Illinois Number 6 and 2.3 million dollars for operation on Montana Rosebud. The upgrading of single quench wastewater quality from Illinois No. 6 by application of reverse osmosis to attain comparability with the two stage quench was indicated to be cost ineffective. With Montana Rosebud the capital cost estimates indicated that there was potential for upgrading single quench water quality or for disposal to pond evaporation. Pond evaporation of single quench would feature a loss of the value of the second stage quench as makeup to reuse circuits. Pond evaporation was not evaluated for Illinois No. 6 operation inasmuch as it is not a viable alternative for the Eastern U.S.

A comparison of estimated annual costs is given in Table 6 for single stage and two stage quench systems with equalized reuse potential. Equalized reuse potential is taken as the separation of a reverse osmosis concentrate

Table 3: Effect of Treatment on Condensate Characteristics Illinois No. 6 - Air Blown

	Raw	Condensate	te	Condensa	ite After	Condensate After Stripping	Biotre	Biotreated Condensate	ensate
Component	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench	Single Ouench	10% Ouench	Final Ouench
H ₂ 0 gal/ton coal	292	30.1	262	293	33	261	294	34	259
NH3, mg/l	5310	10880	4671	20	52	20	77	. 70	
CO2, mg/l	10740	360	11790	5	S	ט רכ	r r	† 7	74
H2S, mg/l	350	44	63	5	S.	വ	0.1	-	ר
HCl, mg/l	2110	20480	~	1	1	' ' ~	· ; ;	• •	-
HF, mg/l	104	1000	1.3	ı	ı		ı	l I	ı
CN, mg/1	20	0.61	51	15	0.15	. <u> </u>	~	ە 1 C	1 (
SCN, mg/l	260	3.2	275	171	1,9	771) C	7.0	3.0
Phenol, mg/l	3329	2209	3640	2640	1630	2920	0.1	7 0	בי
						•		-	
Н	7.1	5.8	7.2	8-10	8-10	7-9	7.7	7.8	7.1
NaCl, mg/l	1	ı	ı	3460	29100	t	3380	29200	
NaF, mg/l	1	t	1	230	1860	ı	219	1870	- 2
504, mg/1 TSS ===/1	1	ı	1		ı	•	282	14	291
155, 111g/ 1 To±21 Fourthers 6	:	,					25	25	25
iotai Equivalent Strong Electrolyte, mg/l as NaCl	trong Eleci	trolyte, n	ng/las Na(<u></u>			4028	31800	359

1.0

89

11.3

Concentration Ratio

Table 4: Effect of Treatment on Condensate Characteristics Montana Rosebud - Air Blown

Biotreated Condensate	10% Final Quench Quench	13.8 109	4 31	1	0.1 0.1	1	1	0.7 4.8	2 10	0.1 0.1	7.6 7.1	8702	1145 1	43 458	25 25	10350 561	18.4 1.0
Biotre	Single Quench	123	40	ı	0.1	ı	ı	4.8	01	0.1	7.5	976	128	447	25	1649	2.94
Condensate After Stripping	Final Quench	109	20	5	5	<u>~</u>	0.07	24	279	5824	7-9	ı	i	1	ı		
te After	10% Quench	13.4	51	Ŋ	5	ı	ı	0.93	11	3637	8-10	8619	1134	ı	ı		
Condensa	Single Quench	123	20	5	5	•	ı	24	270	5056	8-10	996	127	3	t	as NaC1	ion Ratio
a)	Final Quench	Ξ	12730	29270	225	^	^	80	1	7239	7.6	ı	ı	ı	ı		Concentration Ratio
Condensate	10% Quench	13.0	4866	1888	75	5718	574	3.2	91	4675	6.8	ı	i	1	ı	ectrolyte,	٥
Raw	Single Quench	124	11990	27110	199	109	09	78	410	6299	7.5	ŧ	1	1	•	t Strong El∈	
	Component	H ₂ O gal/ton	NH3, mg/l	CO ₂ , mg/1	H2S, mg/l	HC1, mg/1	HF, mg/l	CN, mg/1	SCN, mg/l	Phenol, mg/l	Hd	NaCl, mg/l	NaF, mg/l	504, mg/l	TSS, mg/1	Total Equivalent Strong Electrolyte, mg/l	

Estimated Capital Cost Differences for Single and Two Stage Quench Systems Table 5

		Illinois No. 6	9.6	Montana Rosebud	pnqası
		Single Quench MM\$	*Two Stage Quench MM\$	Single Quench MM\$	*Two Stage Quench MM\$
	1. Gas Cleaning & Cooling	8.40	9.50	4.00	5.50
2.	Condensate Stripping & Biotreatment	7.20	8.30	5.50	6.30
	Sum of 1 & 2	15.60	17.80	9.50	11.80
3	Two Stage - Single Stage		+2.20		+2.30
	Difference with Effluent Equalized by:				
4.	Reverse Osmosis	+0.50			+0.70
5.	Pond Evaporation	NA	NA	0	0

*Condensate from first stage quench = 10% of input gas moisture

Table 6

Estimated Annual Cost Differences for Single Stage and Two Stage Quench Systems with Equalized Reuse Potential

		Illino	Illinois No. 6	Montana Rosebud	osebud
Cos	Cost Component	Single Quench \$/yr	*Two Stage Quench \$/yr	Single Quench \$/yr	*Two Stage Quench \$/yr
¥.	A. Quench & Condensate Treatment Operation @ 2.25 men Maintenance @ 1.0% of Capital Cost Miscl. LS Capital Recovery @ 20%		45,000 22,000 5,000		45,000 23,000 5,000 140,000
a.	Reverse Osmosis Operation & Maintenance Capital Recovery @ 20%	330,000 100,000		110,000	
	Subtotal	430,000	72,000	110,000	213,000
	Excess Annual Cost	358,000			103,000

*Ten percent of gas moisture condensed in first stage.

reverse osmosis operating on lillhors No. 0 coul 15 more as 360,000 dollars per year than a two stage quench system. The finding is con-

sidered characteristic of high halide coals.

With Montana Rosebud coal, the analysis in Table 7 suggests that the two stage quench system is more expensive by about 100,000 dollars per year than the single quench system plus reverse osmosis. The finding is considered characteristic of low halide coals that yield a small volume of condensate.

DISCUSSION

The applicability of a gas cleaning system using a two stage quench to effect preliminary absorption of halides has been indicated to be technically feasible. The process objectives of capture of particulates, absorption of strong electrolyte gases and efficient demisting in the first stage quench were attainable by application of conventional process technology. The objective of control of the unit volume of first stage condensate was feasible by engineered application of a variable level first stage tar decanter. The analysis of benefits of the two stage quench are considered conservative inasmuch as the analysis was based primarily on absorption of HCl and HF. In actuality, the isolation of the secondary condensate from contact with flyash and volatilized salts would increase the contrast between the quality of primary and secondary condensates. The quality of the secondary condensate is expected to be far superior to the primary condensate. The combination of steam stripping and biotreatment of the condensate from the second stage quench is indicated to produce an effluent of low dissolved solids content. It is evident that the low dissolved solids effluent would be amenable to reuse as service water to the coal conversion process with substantially less upgrading. than comparably treated condensate from a single stage gas cleaning process. Parenthetically it should be recognized that activated sludge effluents from treatment of coal conversion wastes characteristically contain low concentrations of organic matter - including some dark color bodies, so supplementary treatment would be required for some reuse applications.

The formation of thiocyanate during two-stage quenching is an enigma that was not resolved in the study. Appreciable thiocyanate is usually present in condensates from single stage quenching of producer gas and coke oven gas. It is established that thiocyanate can form as a result of reaction of free cyanide with sulfur, organic sulfur or oxidized inorganic sulfur (6) (7) (8). The dilemma in two-stage quenching is the estimation of the extent of thiocyanate

formation in the second stage quench.

In two-stage quenching, the first stage quench cooled the gas to the 230-280° F range depending on the specific situation. It can be speculated that thiocyanate formation may occur in the first stage inasmuch as oxidized sulfur would be absorbed, and particulates bearing free sulfur and possible catalytic properties would be removed. Thiocyanate formed in the first stage quench would be removed from the process with the high electrolyte purge and would not register as electrolyte in the condensate from the second stage quench.

Thiocyanate formation in the second stage quench would be favored by the presence of organic sulfur, ammonia and cyanide as well as by temperature conditions. The limited availability of oxidized sulfur or external oxidant would presumably restrict reaction between cyanide and sulfide. However, reactions

from the second stage quench were sufficient to cover the situation. It is conceivable that lower concentrations would be realized in practice -- which

would register as improved quality of second stage condensate.

Absorption of HCl and HF in the first stage quench was assured by installation of a sieve tray absorber in conjunction with the venturi scrubber. The sieve tray absorber was the principal gas train component in the cost differential between single stage and two-stage quenching. It follows that cost savings would be realized if the combination of venturi scrubber plus efficient mist eliminators could be experimentally verified as adequate from the standpoint of absorption. Absorption of HF was indicated to control the design of the absorption system. Efficient mist elimination between first stage and second stage quenches is essential.

The cost estimates were prepared on the basis of carbon steel vessels and tanks in the gas train. The high electrolyte concentration of condensate from first stage quench, combined with suppressed pH, could necessitate the application of special corrosion resistant materials. Consultation with chemicals industry design engineers produced the recommendation of titanium clad vessels and tanks. Consultation with coke byproduct plant design engineers produced the recommendation of carbon steel with the expectation that the units would be tar coated. The position of the author is that the materials situation warrants experimental investigation including the possible application of neutralization in conjunction with corrosion inhibitors. A requirement for exotic materials would compromise the cost analysis presented herein.

The applicability of biological treatment to the wastewater was assumed inasmuch as coke and gas house liquors have been biologically treated for over 40-years. However, it is also recognized that problems have been experienced with biological treatment of some coal conversion process wastes, especially when the electrolyte concentration was high (9). For study purposes it was assumed that treatment problems could be resolved by process modifications to suit the specific situation. Some reservation is also expressed regarding the applicability of reverse osmosis to substrates containing a variety of non-specific organic compounds. The record of the process is spotty for such applications, but some latitude is available by process modification.

CONCLUSIONS

The following conclusions were developed during the course of the study:

- l. The concept of preliminary absorption of halides and other strong electrolytes in a low volume primary condensate was indicated to be technically feasible for the gasification system studied. The essential features of the first stage quench are particulate removal, strong acid gas absorption and mist elimination. The technology is considered to be widely applicable to coal conversion processes employing wet gas cleaning.
- 2. The two stage quench system was indicated to be economically favored as compared to reverse osmosis desalination of single stage condensate where the gasifier gas contains high halide content and/or high moisture content.
- 3. Thiocyanate in the secondary condensate was indicated as a possible limitation to water quality that was not quantified in the study.

The study results reported herein represent the accomplishments of many individuals on the staff of Arthur G. McKee and Company and elsewhere. Particular recognition is due: Dr. K. C. Vyas, Lead Alternate Fuels Engineer; K. J. Kosinski, Project Process Engineer; and E. S. Hayes, Project Estimator.

Valuable assistance was also contributed by Dr. G. D. Case and A. S. Moore, Jr. of the Morgantown Energy Technology Center and by Dr. Fred E. Witmer, Technical Project Officer, Division of Environmental Control Technology, DOE. The study was performed under Contract EE-77-C-02-4375 with the Division of Environmental Control Technology, Department of Energy.

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GRAND FORKS ENERGY TECHNOLOGY CENTER

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INTRODUCTION

Environmentally related studies of slagging fixed-bed gasification at the Grand Forks Energy Technology Center (GFETC) were initiated in 1976. A principal factor involved was the availability of a pilot-scale fixed-bed gasifier which could be quickly restored to operational status. Initially the pilot plant and gasifier was constructed and operated under the Bureau of Mines during the period 1958-1965 to demonstrate the feasibility of slagging operation and the parameters involved. The major objectives of the reactivated project are to develop: 1) a scaleable process data base on feed/ product material balance, and 2) a detailed environmental assessment of the slagging fixed-bed gasifier (SFBG) process. The pilot plant has been operated in its original configuration for two years, however, plant and gasifier capabilities will be significantly expanded by modifications which are currently in progress. When modifications are completed and operation resumed, information will be obtained on a variety of test coals, including both low-rank non-caking coals (lignites and subbituminous) and bituminous coals with a range of caking characteristics.

The environmental assessment will include extensive sampling and analyses of process streams to characterize gaseous, solid, and liquid effluents, and testing of pilot plant-scale simulations for treatment of liquid effluents to establish the feasibility of zero discharge of liquids and safe disposal of solid wastes. The objectives of the GFETC project directly support the application of the slagging fixed-bed gasification technology to commercial development. The 25 ton/day gasifier has, at present, the unique capability of generating coal-specific data at reasonable cost for the large number of candidate U.S. coals.

In the particular area of liquid effluents and their treatment, a major part of the assessment performed on the SFBG is believed to be substantially applicable to fixed-bed, dry-ash gasifiers proposed to be used in first generation SNG plants. This will be validated, if possible, through comparative tests or bench-scale simulations. The GFETC gasifier can then provide information desired by the public on specific feed coals proposed for dry-ash SNG projects and industrial applications.

DESCRIPTION OF PILOT PLANT FACILITIES

The gasifier at the Grand Forks Energy Technology Center is a pilot-scale version of a conventional pressurized fixed-bed gasifier. In the commercial "dry-ash" process, gasification temperatures are maintained sufficiently low by the use of excess steam to allow removal of the ash in

to dry-ash removal operation. The steam consumption per unit of coal gasified in a slagging gasifier is about one-fourth of that required for a dry-ash unit, while at the same time, the gas production capacity per unit cross-sectional area is as much as three or four times that of the dry-ash gasifier.

Figure 1 is a cross-sectional view of the original GFETC gasifier. Coal is batch-charged to a lock hopper and gravity feeds into the main body of the gasifier. The coal is heated by the countercurrent flow of hot gases. As it descends, coal is first dried and then carbonized. At the hearth area, only a residual char composed of carbon and ash remains. The oxygen/steam mixture is admitted through four tuyures just above the hearth, where the gasification and combustion reactions occur. Temperatures at the hearth are sufficiently high to maintain the ash in a liquid state, and the molten ash drains through a centrally located taphole into a water quench bath. A slag is produced which resembles coarse sand. It settles to the bottom of a water-filled lock hopper and is periodically removed.

The flow diagram of the pilot plant system is shown in figure 2. The hot gases pass up through the fuel bed, heat the coal, and carry the tar, light oil, water vapors, and the gas produced during carbonization to the gas offtake. The product gas stream is, therefore, a mixture of desired gas plus a variety of condensibles and other components. This stream enters a washer where a spray of the aqueous fraction of gas liquor which is recycled and cooled condenses water, light oil, tar vapors, and removes entrained dust particles. Accumulations in the spray washer are periodically discharged. The gas is then cooled, depressurized, and passed through a coke-filled scrubber for final cleanup before it is metered. Up to 1 ton/hr of lignite can be gasified in the unit at a 400 psig operating pressure.

The objectives and capabilities of the GFETC pilot plant program were expanded beginning in early 1977. Two major changes are involved. The pilot plant and gasifier are being modified to provide the capability to: 1) operate continuously for periods of 5 to 7 days, and 2) to test agglomerating coals. Design of additions or modifications to existing facilities of the Center was initiated, and construction phases are in progress. The gasifier will be relocated in an addition to the existing pilot plant in which a centralized control room and laboratories for effluent-related functions will be provided, and a conveyor system for unmanned coal charging of the gasifier is being installed.

Modifications to the gasifier include: installing a stirrer which operates in the top portion of the bed, and providing a double coal lock charging system with feeders. A cross-sectional view of the modified gasifier is shown in figure 3. Auxiliary additions include gas liquor separation, storage, and incineration, and a nitrogen supply purge system. A schematic of the modified pilot plant system is shown in figure 4. A conceptual drawing of the gasifier and facility is shown in figure 5.

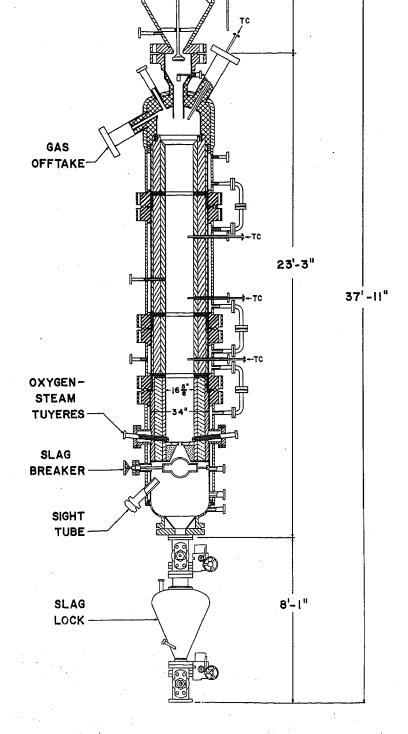
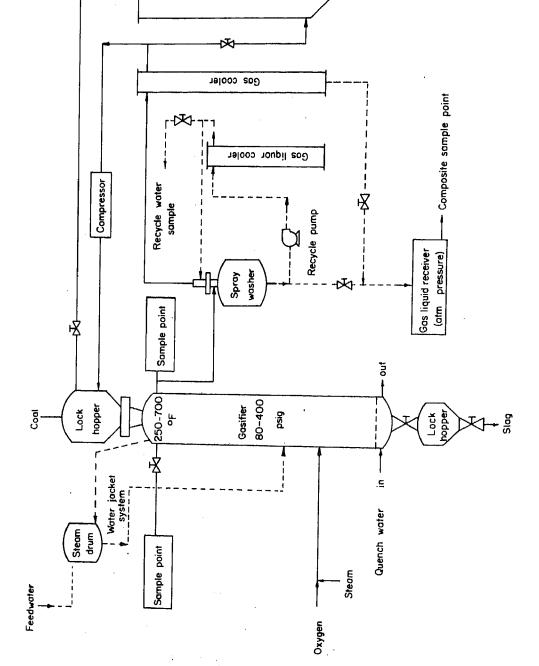


Figure 1. - Cross section of original GFETC slagging gasifier. Configuration used until September 1978.



- Process flow diagram for the GFETC slagging gasification pi Figure 2.

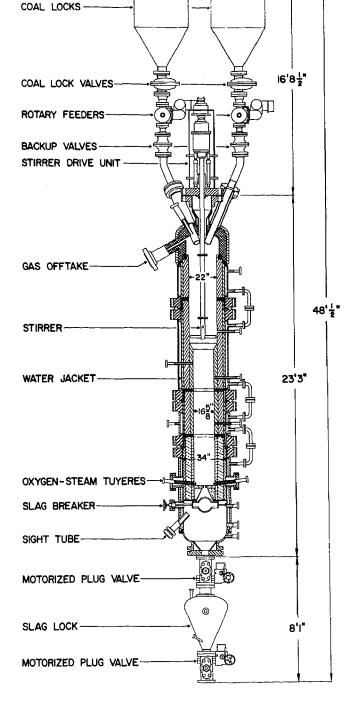


Figure 3. - Cross section of modified GFETC slagging gasifier.
Operation planned for early 1979.

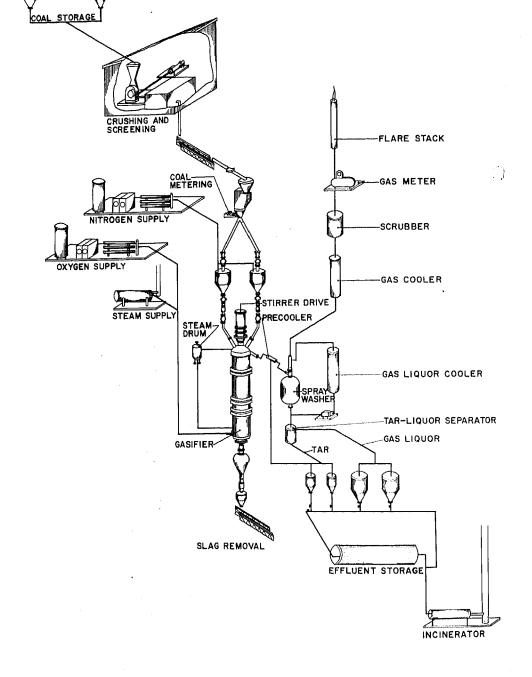


Figure 4. - Schematic of modified GFETC pilot plant.

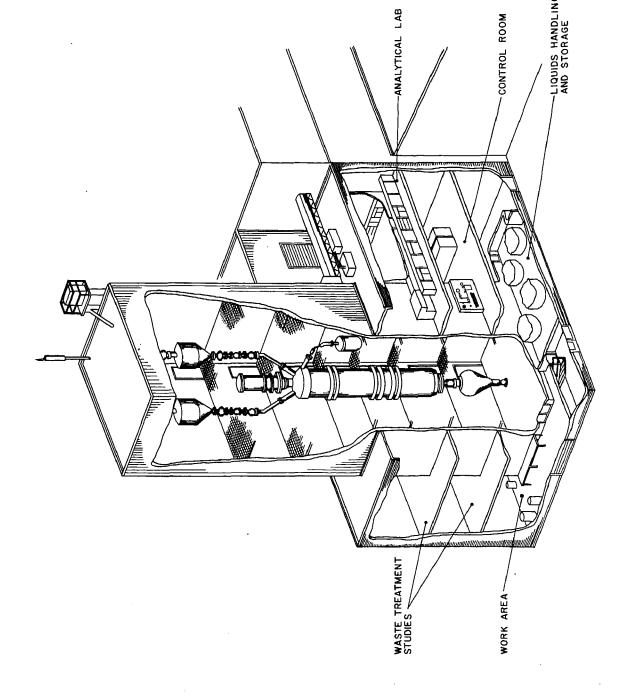


Figure 5. - Conceptual view of relocated SFBG and associated facilities.

must be reduced prior to entering the spray washer. The precooler will also selectively remove tars and heavier components in the product gas when the lower moisture coals are used.

3. STRATEGIC APPROACH FOR ENVIRONMENTAL ASSESSMENT

The selective approach of the GFETC project is that the primary contribution which data from this oxygen-blown gasifier can make is to the direct application of SFBG technology in SNG plants. The information is expected to be used by future designers and operators, as well as state and federal agencies which are charged with licensing and regulating these plants. Data on specific coals will be made available to the public on gas contaminants, and process-produced tar, oil, and waste water. Since the principal unresolved and controversial problems attending operation of SNG plants are concerned with the treatment, use, and disposal of tar, oil, and waste water, studies will be performed to establish treatment techniques consistent with total reuse of water and zero discharge of liquids.

The gas liquors from the SFBG process are produced from the moisture in the raw coal and any process steam not reacted, the tar and oil originating from carbonization of the coal, plus a variety of organics and inorganics which are dissolved in the aqueous condensate. The process streams that result from treatment of gasifier effluents are device-specific -- that is, they depend on the particular hardware that is used. The treatment operations have, therefore, been designed to provide enough flexibility to ensure scaleable data, even in cases where specific hardware used may not be the type selected for future commercial application.

The treatment steps for the aqueous phase currently planned involve: 1) ammonia stripping, 2) phenol extraction, and 3) biological treatment. In addition, it is planned to study the suitability of waste water from various stages of treatment in a simulated cooling tower, the degree of oxidation or evaporation of residual organics, and the fouling of heat transfer surfaces. Studies relating to the tar-oil fraction include characterization and suitability for potential utilization schemes.

The product gas is extensively characterized and analyzed. Studies of gas treatment are underway elsewhere which address points of particular concern (e.g., studies on methanation at the Synthane Plant and at IGT), and the commercial technology is judged satisfactory with minimum refinement. For these reasons gas treatment is not being studied.

Solids produced in a commercial slagging gasification plant would include slag and a variety of sludges produced in water treatments. Slag from the pilot plant will be characterized in respect to analysis and leachability. Sludges, as they are produced in various pilot plant phases of the treatment studies, will be evaluated for potential disposal or utilization.

4. SAMPLING AND ANALYTICAL METHODS FOR GASEOUS AND LIQUID EFFLUENTS

A major effort has been directed to developing and enlarging the capabilities for characterization of the gaseous and liquid effluents produced. In general, established techniques are verified and progressively modified to the process-specific conditions which exist.

Samples of offtake gas are collected regularly and routinely during operation and analyzed by gas chromatograph with a thermal conductivity detector. The instrument is calibrated with standard gases for: hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen sulfide, ethene, ethane, propene, propane, iso-butane, and normal-butane. Approximately 20 additional hydrocarbons are indicated by GC analysis with a flame ionization detector. These components are being identified, and their determination will become routine. Sulfur gases, hydrogen sulfide, carbonyl sulfide, carbon disulfide, sulfur dioxide, and thiophenes, etc. are analyzed by separate GC with flame photometric detector. Methods are being developed for routine determination analysis of hydrogen cyanide, thiocyanate, and ammonia.

The major effluent stream of interest is the condensible fraction of the product gas -- the water and organics removed from the product gas stream in the gas quenching system. Obtaining representative and reliable scaleable samples has been a principal concern in present studies. Three different sampling methods are used. Method I consists of sampling the total quantity of liquids accumulated in the spray washer during each test. Degradation of certain chemical constituents due to system residence time, dilution effects due to the startup water in the spray washer, the effects due to high recycle rate of aqueous fraction, and the inability to collect samples representative of selected time periods are all problems of this method. Method 2 utilizes sampling systems which take a slip stream of the product gas at the gasifier offtake and pass it through a series of cyclones, condensors, and filters to remove the condensibles and particulates from a measured quantity of gas. Continued refinements have been made to solve the problems of sampling a dirty, high-pressure gas stream and to overcome inherent deficiencies associated with Method 1. The specific objective is to provide the capability to collect a reproducible, scaleable representative sample during selected short-time periods of operation.

Method 3 is a different approach to characterizing the production rate of the condensible effluents. It utilizes a gas chromatograph for on-line analyses. The technique being developed performs a simulated distillation of the coal tars produced with the product gas at intervals of 5 minutes. Identification of compounds by groups is being studied and appears to be feasible. This system is demonstrably capable of establishing rapid and short-term variations in tar-oil production rate, and possibly defining composition changes during short-term process upsets.

addition, organic compound identification by high-pressure liquid chromatography, pyrolysis GC/IR, NMR, and UV/Vis spectrophotometry is in progress and will greatly enhance the characterization efforts.

The aqueous phase of gas liquors normally contains ammonia, phenols, and acid gases. Ammonia and phenol are present at concentrations as high as several thousand mg/l. Routinely, the pH, alkalinity, phenol, o and m-p-cresol, ammonia, cyanide, sulfide and total sulfur, total organic carbon, and inorganic carbon content of aqueous phase is determined. Analytical development efforts are currently directed to the determination of trace organics present in the aqueous liquor fractions and as these techniques are established, will be added to the routine analytical base.

Determination of major, minor, and trace elements in effluents in order to establish material and elemental distribution in coal gasification is planned. Data will be reported for selected trace elements, including the following: antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, germanium, lead, lithium, manganese, mercury, molybdenum, nickel, phosphorous, selenium, strontium, tellurium, tin, uranium, vanadium, zinc, and zirconium. Facilities of the Center include an ICAP analyzer for trace element determinations. At present, verification of procedures for sample preparation and processing are in progress and first efforts on selected samples have been initiated.

5. RESULTS TO DATE ON CHARACTERIZATION OF GASEOUS AND LIQUID EFFLUENTS AND RELATIONSHIP TO OPERATING VARIABLES

Since May 1976, and until September 27 of this year, a total of 66 tests were scheduled with the Grand Forks pilot plant. Feedstock included three lignites and two subbituminous coals ranging in moisture content from 20 to 40 pct. Sustained operation was not achieved in the limited tests on subbituminous coals due to slagging problems or on one lignite of 40 pct moisture content due to the high moisture content. Samples and data in regard to effluent characterization were collected in 30 of the tests, principally on lignite from two mines, Indian Head (Mercer County, Central North Dakota) and Noonan (Burke County, Northwest North Dakota). Pressure was varied from 100 to 400 psi in 100-pound increments, and oxygen flow from 4000 to 6000 scfh, with corresponding steam inputs from 0.9 to 1.1 molar ratio of oxygen to steam.

Progressively, sampling techniques have been modified and refined, and efforts were directed to establishing test reproducibility, operational stability, and variability, particularly during upsets caused by coal charging. Samples from a variety of sampling locations and utilizing different techniques were systematically collected for comparison. Concurrently, analytical methods and techniques have been and continue to be progressively verfied and modified as required.

ment studies now underway at two facilities, and extensive effort was made to establish progressive changes in effluent characteristics as a function of operating time. Special effort was also made to determine change which occurred in effluent characteristics during the periodic upsets caused by coal charging and interruption of coal feed. These factors will be much less important in the modified gasifier when test periods of longer duration are possible, and the periodic upset during charging the single lock hopper will no longer occur. However, these data are required in establishing and assessing the validity of data collected in the program to date.

Since termination of operations at the end of September, efforts have been directed to compiling and evaluating the data. Typical fuel analyses for test lignites are given in Table 1. Moisture content of Noonan lignite "as tested" is not representative of the "as received" condition of 36 pct due to moisture loss which occurred in extended open storage, size preparation, and handling over the duration of the test operation. Data given in Table 2 illustrate the composition of gas produced. Both iso-butane and n-butane are now determined and found to be at the 0.01 to 0.02 pct range for gas produced from Indian Head lignite. Operating results at pressures ranging from 100 to 400 psig are given in Table 3. Effluent production of selected components in gas liquor as a function of operating pressure is given in Table 4. Effluent production and characteristics at identical operating conditions are compared for two lignites in Table 5. It is expected that when operations are resumed in the modified gasifier, tests will be conducted on test lots of the same lignites to compare results obtained with double lock feeding to those obtained with single lock operation.

A variety of publications and presentations have been prepared at the GFETC describing general and selected phases of the studies. These are listed as a source of additional information at the end of this paper.

6. PLANS FOR SEPARATION AND TREATMENT OF LIQUID EFFLUENTS

In the past, gas liquor that accumulated in the spray washer was periodically sampled and discharged to an external tank at atmospheric pressure. On completion of a run, all remaining liquor was drained to this tank. Tar, oil, and aqueous phases were decanted and drawn off separately, sampled, and analyzed. The composite end-of-run sample contained the liquor produced during the run and the startup city water required for initial operation.

The composite gas liquors contain an aqueous phase, a floating oil phase, possibly a sinking tar phase, and solid particles of dust, ash, and ungasified coal. Two improvements of the sampling and gas liquor collection system are being planned. The first involves continuous drawoff from the spray washer of two or three different phases—floating oils, heavy (sink) tars, and the principal aqueous phase. Secondly, a precooler will be installed between the gasifier and the spray washer with limited injection of

Proximate, pct:

Moisture Volatile matter Fixed carbon Ash	37.6 25.7 30.5 6.2	30.3 28.2 35.4 6.1
Ultimate, pct:		
Hydrogen Carbon Nitrogen Oxygen Sulfur Ash	6.9 40.9 .5 44.7 .8 6.2	6.4 45.9 .7 40.6 .3 6.1
Heating value, Btu/lb	6780	7670
Ash Fusion Temp., °F:		
Initial deformation Softening Fluid	2030 2080 2130	2070 2100 2130

TABLE 2. - Typical product-gas analyses

Coal Run Number	Noonan RA-31	Indian Head RA-40
Gas Analysis, pct, N ₂ free:		
CO. H2. CO2. CH4. C2H4. C2H6. C3H6. C3H8. H2S.	57.3 30.5 6.4 5.1 .2 .3 .09 .09 .1	53.6 32.5 8.4 4.9 .2 .3 .06 .04
Heating value, Btu/cu ft	340	333

Loal	Indian Head			
Moisture in Coal, pct	22.9	36.4	35.7	38.6
Test Conditions: Oxygen rate, std.cu.ft./hr Oxygen/steam molar ratio Calculating period, hr	4,000 1.0 7.15	4,000 1.0 6.08	4,000 1.0 11.92	4,000 1.0 8.68
Fuel Rate (as-charged), lb./hr	1,049	1,233	1,259	1,296
Fuel Rate (maf), lb./hr	729	703	730	728
Product Gas Rate, std.cu.ft./hr	20,108	20,759	21,994	21,039
Slag Rate, lb./hr	72	55	67	50
Oxygen Consumption:				
cu.ft./1000 cu.ft. gas	198.9	192.7	181.9	190.1
cu.ft./1000 cu.ft. CO + H ₂	224.0	218.7	212.3	230.3
cu.ft./lb. maf fuel	5.49	5.69	5.48	5.49
Steam Consumption:				
lb./1000 cu.ft. gas	9.45	9.15	8.64	9.03
1b./1000 cu.ft. CO + H2	10.64	10.39	10.08	10.94
lb./lb. maf fuel	.26	.27	.26	. 26
Production, cu.ft./lb. maf fuel:				
Gas	27.58	29.52	30.11	28.89
CO + H ₂	24.50	26.01	25.80	23.85
Product Gas Composition:				
co ₂	5.0	6.6	8.4	10.5
Illuminants	.6	.3	.3	.2
Н2	29.2	31.3	31.5	28.5
co	59.7	57.0	54.2	54.4
С2Н6	.2	.3	.3	.3
СН4	4.3	4.5	5.3	6.1

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Run Number	RA-18	RA-36	RA-33	RA-38
Pressure, lb/sq in	100	125	200	400
1b/ton MAF Coal:	•			
Tar Water Ammonia TOC	92	83	73	66
	1,044	1,404	1,408	1,378
	7.8	9.1	9.6	12.7
	10.0	11.4	12.3	12.9

water to condense tar, but without condensing the aqueous fraction. This precooler will be particularly important in operating on low-moisture (bituminous) coals where the offgas from the top of the gasifier may reach 900° F rather than the 320° F associated with lignite of 30 pct moisture.

The individual phases of the gas liquor must be separated for subsequent treatment. The aqueous phase of gas liquor, with tar and oil essentially removed, contains some suspended matter of colloidal tar/oil, dust, ash, and unburned coal. Ammonia and phenol can be removed by biological action, but past experience has shown that equipment size to provide required time generally precludes biological treatment of these substances at high concentrations. Both ammonia and phenol have market value, and proven commercial processes can successfully recover these from the gas liquor. Studies relating to development of improved techniques for their removal, therefore, have been given a low priority. Sour gas stripping and phenol extraction are being considered, however, as a means of producing representative waste water for biological treatment studies, both before and after phenol and ammonia removal. Although most investigations have been on aerobic digestion, anaerobic biological treatment offers some advantages and will also be considered.

Various physical/chemical processes, such as chemical and polymer coagulation and precipitation, multi-media filtration, activated carbon adsorption, ultra filtration, reverse osmosis, etc., are also candidate treatments to upgrade water qualities from gas liquor. Bench-scale experiments will be performed on selected methods to ascertain their applicability to the SFBG liquors, both as a primary treatment or as a polishing technique.

The major use of treated water at proposed gasification plants is in cooling towers. From an economic standpoint, the less treatment gas liquor requires prior to use in a cooling tower, the better. In any case, removal of tar, oil, and the major portion of the phenol and ammonia would be required prior to use of liquor in a cooling tower. A small pilot-scale cooling tower is being considered to operate on gas liquors as produced in

Run Number Coal Moisture in Coal, pct Operating Pressure, lb./sq.in	RA-31 Noonan 30.3 200	RA-40 Indian Head 34.7 200
Production, lb./ton_maf:		
Tar	90	70.2
Water	1,140	1,220
Ammonia	12.6	11.0
Total organic carbon	13.3	12.3
Concentration of Selected Constituents in Aqueous Phase:		
рН	9.3	9.5
Alkalinity, ppm CaCO3	30,020	25,410
Ammonia, ppm	10,220	8,440
TOC, ppm	10,000	9,460
Phenol, ppm	5,689	4,260
o-cresol, ppm	1,000	836
m-p cresol, ppm	3,317	1,671
Concentration of Selected Components in Tar Phase, pct:		
Phenols	18.2	15.4
Naphthols	3.9	5.6
Dihydroxybenzenes	1.4	0.0
Naphthal enes	9.3	9.0
Aromatic hydrocarbons with 3 to 5 rings	8.5	8.2
Saturated hydrocarbons	10.2	22.0
Non volatiles at 300° C and 0.1 torr	2.4	3.6
Average mol. wt. of volatile compounds	152.2	156.9

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7. SOLID AND SLUDGE EFFLUENTS

In a commercial coal gasification plant the slag, or ash produced, is a formidable quantity of material. For example, a 25,000 ton/day lignite facility may produce 2,000 tons/day of slag/ash which must be disposed of. Except for possible use as an aggregate or as a fill for leveling purposes, the probable disposal method for the slag is in a landfill, and most likely it will be returned to the mines from which the coal came. Slag produced in SFBG is believed to be not leachable, but if process water is used for quenching, it may contain leachable components. As leaching to groundwater is not permitted by regulatory authorities, either an extensive sealing operation will be required or the slag, as produced, must be shown to be essentially non-leaching.

The disposal of residual dissolved and suspended inorganic and organic solids from the various waste water processing and treatment streams must also be managed to prevent contamination of surface or groundwater or the atmosphere. It has been suggested that sludges produced may be valuable as soil conditioners and low-grade fertilizers in mine spoil bank revegetation programs.

Blowdown from a cooling tower will be high in dissolved (and possibly suspended) solids which must be disposed of. Some materials in the blowdown may be inherently toxic, as are cadmium and mercury, or they may be merely aesthetically unpleasant, as is iron. Other elements, such as sodium, calcium, and magnesium, may contribute undesirable qualities for use in irrigation, domestic, or industrial water uses. Evaporation of cooling tower blowdown will probably be necessary, either in an evaporation pond or by direct means using waste heat.

The characterization of these solids and wastes will continue at GFETC. Expansion of SFBG studies will utilize, to a large extent, established and on-going programs to characterize the leachability of such wastes and to develop other necessary information.

8. CONTRIBUTION TO ASSESSMENT OF BIOMEDICAL EFFECTS

The gasification of coal produces some materials which have been shown to have toxic and mutagenic effects. Inevitably, small amounts are released to the atmosphere or are brought into contact with workers in a gasification plant. The Grand Forks slagging gasifier pilot plant is a reasonable model for worker exposure, and it provides data that, with proper interpretation, permit environmental emissions to be estimated. The biomedical concerns have generated a large scientific effort. Using a variety of procedures, skin tests, inhalation tests, and gross toxicology, by ingestion and tissue analysis with appropriate test animals, and bacterial mutagenicity, the

In addition, health records will be maintained on workers engaged in coal processing activities at the Grand Forks Energy Technology Center to assist in determining any possible long-term effects relating to occupational exposures.

9. CONCLUSION

The SFBG at GFETC provides the opportunity to assess the environmental effects of fixed-bed coal gasification. Utilizing manageable test lots of coal, representative effluents will be generated for verification of treatment and control processes or development of improved techniques. The capabilities and potential of the modified pilot plant will expand the operational and environmental data base available for commercial development of a viable SNG industry in the U.S.

10. GFETC PUBLICATIONS ON THE SFBG

- 1. Gronhovd, et al. "Design and Initial Operation of a Slagging Fixed-Bed Pressure Gasification Pilot Plant." U.S. Bureau of Mines Report of Investigations 6085.
- Gronhovd, et al. "Slagging Fixed-Bed Gasification of North Dakota Lignite at Pressures to 400 PSIG." U.S. Bureau of Mines Report of Investigations 7408.
- 3. Ellman and Johnson. "Slagging Fixed-Bed Gasification at the Grand Forks Energy Research Center." Eighth Synthetic Pipeline Gas Symposium, Chicago, 1976.
- 4. Ellman and Schobert. "Pilot Plant Operation of a Fixed-Bed Slagging Gasifier." 173rd National American Chemical Society Meeting, New Orleans, 1977.
- 5. Schobert, et al. "Petrochemistry of Coal Ash Slags. 1. Formation of Melilite and a High-Temperature Glass from a Calcium-Rich, Silica-Deficient Slag." Joint CIC-ACS Conference, Montreal, 1977.
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- 7. Ellman, et al. "Current Status of Studies in Slagging Fixed-Bed Gasification at the Grand Forks Energy Research Center." Ninth Biennial Lignite Symposium, Grand Forks, 1977.

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- 11. Schobert, Johnson, and Fegley. "Carbonization Reactions in the Grand Forks Slagging Gasifier." 176th National ACS Meeting, Miami, 1978.
- 12. Mayer, Olson, and Schobert. "Standard Methods" for the Analysis of Coal Gasification Effluents--Caveat Emptor." National CIC Meeting, Winnipeg, 1978.
- 13. Olson and Schobert. "Evaluation of Methods for Determination of Sulfide in Coal Gasification Waste Water." 176th National ACS Meeting, Miami, 1978.
- 14. Olson and Schobert. "Production of C₁-C₄ Hydrocarbons in the Gasification of Some North Dakota Lignites." North Dakota Academy of Science Meeting, Grand Forks, 1978.
- 15. Ellman, Johnson, and Fegley. "Studies in Slagging Fixed-Bed Gasification at the Grand Forks Energy Technology Center." Tenth Synthetic Pipeline Gas Symposium, Chicago, Illinois, 1978.
- 16. Johnson and Fegley. "Gasification of North Dakota Lignite in a Slagging Fixed-Bed Gasifier." 71st Annual Meeting, AIChE, Miami Beach, Nov. 1978.

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ABSTRACT

An historical account of the development and current studies of environmental monitoring and compliance at the SYNTHANE pilot plant will be presented. This account will include the experiences and problems in establishing monitoring programs in the following areas:

Air:

Ambient Monitoring Stack Testing Fugitive Emissions Noise:

Background In Plant

Water:

Surface Water Control
NPDES* Sampling
Continuous Water Monitoring
Occupation Health:
Problem and Direction

Solid Waste:

Characterization Disposal

In February and March 1975 the first ambient air background studies were undertaken at the SYNTHANE pilot plant. Subsequent to these initial studies an environmental monitoring and compliance program was developed incorporating the areas noted above. The cost of this program to date plus facilities and equipment amount to approximately three (3) million dollars. The experience provided in interfacing with the technology development and developing the environmental monitoring and compliance program can be of value to all who are involved in small scale and large scale development.

*National Pollutant Discharge and Elimination System.

The Environment & Conservation Division of the Pittsburgh Energy Technology Center, Department of Energy, was formed on July 1, 1975. The charter under which this division operates in the environmental area focuses on the assessment of pollution potential from coal conversion processes and the evaluation of alternative techniques for reducing the environmental impacts of these technologies. This paper presents an overview of the comprehensive monitoring and assessment of the SYNTHANE pilot plant.

As of December 1, 1978, US DOE Headquarters terminated operations at the SYNTHANE pilot plant. Subsequently the majority of the programs discussed in this report have been or will shortly be discontinued. This report will attempt to highlight important considerations in designing and implementing an environmental monitoring program for other pilot plant operations.

The major assessment efforts can be appropriately divided into five areas in which most environmental legislation is also categorized—air, water, noise, solid waste and occupational health.

Process Description

The 72 T/D SYNTHANE Coal Gasification pilot plant converts coal to high BTU synthetic pipeline gas. Basically there are five major steps in the process: (1) pretreatment, (2) gasification, (3) shift conversion, (4) purification, and (5) methanation.

<u>Pretreatment</u>: The coal is crushed to -20 mesh, dried with hot flue gas generated from the combustion of No. 2 fuel oil, then pressurized in lock hoppers with CO₂. It is then pretreated at operating pressure with a steam-oxygen mixture. This mild oxidation destroys the caking properties of the eastern coals so that they do not agglomerate in the gasifier.

Gasification: In the free fall coal feed mode of operation the coal overflows the pretreater into the gasifier, about 20 feet above the normal bed level. The coal falls through the hot gases rising from the fluidized bed and is partially devolatilized. When utilizing the deep bed injection mode the coal is fed below the top of the fluidized bed. In either mode steam and oxygen enter the gasifier just below the fluidizing gas distributor. The gasification reaction occurs in the fluidized bed. Char containing ash and unreacted carbon is transferred to a separate bed in the lower part of the gasifier vessel where it is cooled before being discharged to lock hoppers.

dioxide, and impurities, is passed through a venturi scrubber and a scrubber tower to remove carry-over ash, char, and tars.

*Shift Conversion and Purification: The concentration of hydrogen and carbon monoxide in the gas is then adjusted to a three-to-one ratio in the shift converter by the reaction of CO with steam to produce H₂+CO₂. The acid gases are absorbed in a hot-potassium-carbonate tower (Benfield process); carbon dioxide is reduced to below 2% and sulfur is reduced to 40 parts per million. (Regeneration of the potassium-carbonate solution produces a gas rich in hydrogen sulfide which is converted to elemental sulfur by the Stretford process). The remaining traces of sulfur in the product gas are removed by passing the gas through activated charcoal.

*Methanation: Two systems for methanation of product gas were planned for testing--hot gas recycle (HGR) and tube wall reactor (TWR).

I. Ambient Air Monitoring

A. Background Study

The ambient air monitoring program for the SYNTHANE pilot plant began with an initial background study of the air basin in which the plant was sited. This initial phase was performed in February and March 1976 and served to provide a background data base with which to compare ongoing monitoring data as the pilot plant began operation. The background study consisted of the following data collection activities. The results of these data comparisons are available through the EC Division.

Four Hi Vol samplers were operated for a 24- hour period every six days. The locations are shown in Figure 1. The Hi Vol filters were weighed and analyzed for the following constituents: fine particulates, sulfates, nitrates, mercury, arsenic, nickel, lead, beryllium and cadmium. The prevailing 24-hour surface wind from Allegheny County Airport, located approximately 3.5 miles from the air monitoring network, was computed for each test along with other meteorological dispersion parameters. The data were then compared with all federal and state ambient air standards and analyzed to determine what the plant contribution was to the monitors.

*The Shift Conversion and Methanation process steps were not operated throughout the life of the SYNTHANE pilot plant.

An eight-station sulfation plate network was operated utilizing fifteen-day exposure periods. The sulfation data was converted to PPM SO₂ by dividing the average sulfation rate of three plates located near the continuous SO₂ monitor at Site 1 into the average hourly SO₂ concentration for the fifteen-day period. This number was then converted to ug/m^3 SO₂ by multiplying it by 2620. The data were compared with annual ambient SO₂ standards and then analyzed to determine the plant contribution.

A dustfall network was utilized consisting of eight site locations. The dustfall jars were collected once a month and analyzed for total dustfall, water soluble particles and water particles. The results were compared with Pennsylvania State ambient standards.

In addition to the stationary sites a mobile van sampled the air basin. See Appendix A.

B. Six Month Air Quality Study

The second phase of the air monitoring program conducted August 1976 to January 1977 consisted of a six month study to assess the pollutant contribution of the pilot plant operation to the ambient air. These monitoring data were compared to the background data base to evaluate any change in the air basin. The method of data collection and parameter measurement for the sixmonth study was essentially the same as for the background study.

The pilot plant contributions to the Hi-Vol samplers were determined by plotting the prevailing 24-hour wind for each Hi-Vol unit on a map showing the location of each monitor and the SYNTHANE plant. A triangular area is drawn along the radial of the prevailing wind from the plant. The width of the triangle is a 15° arc on either side of the prevailing wind radial. (Note Figure 1.)

Monitoring parameters included ${\rm CO}$, ${\rm O_3}$, ${\rm NO_x}$, ${\rm SO_2}$, Total Hydrocarbons (THC), ${\rm H_2S}$, Coefficient of Haze (COH), wind speed and direction, dew point and temperature. Under worst case assumptions, the concentrations at any monitoring site within this triangle measure the plant emissions. All other monitoring sites are considered to measure background. The difference between the average downwind concentrations and the average upwind concentration is considered to be the plant contribution. This of course is a worst case assumption which assumes that no other source exists between the plant and the receptor site. Extra care should be taken in interpreting the data with this assumption in mind.

Figure 1 - Ambient air monitoring sites

AIR QUALITY SAMPLING NETWORK

HI-VOL DATA

SULFATES 4 SITE NO FINE PARTICULATES **NITRATES**

DATE: 12/24/76 RUN NO: 25

STRENGTH 2.4 °C GROUND INVERSION TOP 1600 FT. MSL UPPER LEVEL INVERSIO FT. MSL FT. MSL STRENGTH_ BASE TOP

AFTERNOON VENTILATION RATE 6400 M3/g

2-7-79 L-16496A

. Continuous Monittoring Italiers

The background and six-month study provided a data base to evaluate the pilot plant contribution to the ambient air under certain operating conditions. However, the nature of pilot plant operations are such that changing conditions were anticipated to change emission characteristics. Some parameters affecting effluent characteristics include types of coal (high and low sulfur content), temperatures, pressures and fuel feed characteristics.

To properly evaluate these changing conditions, a continuous monitoring network was determined to be most cost effective as well as efficient. Two ambient air monitoring trailers were subsequently sited and put into operation in early 1977. Records containing SYNTHANE pilot plant operations data were maintained to compare with the data generated from the monitoring trailers. The correlation of these two information sources provided a means of evaluating changing process conditions relative to the ambient air.

The Hi-Vol samplers, dustfall jars and sulfation plates were retained from the background and six-month study as part of the continuous monitoring network. The only change in these data collection systems was analysis of the metals on the Hi-Vol filters. These were changed to provide a full survey for all metals potentially emitted from the pilot plant and to correlate them with the source testing.

The site source of the trailers were determined using the meteorological data base of the background and six-month study. The prevailing wind was delineated and one trailer was located upwind and one downwind of the plant. Physical interferences such as buildings, trees and hills were taken into consideration, as well as accessibility.

D. Stack Testing Program

Coordinated with the ambient air monitoring program was a source testing program. The primary emission source on the SYNTHANE pilot plant site was the thermal oxidizer. At the initiation of the program, April 1977, all of process wastewater and gases generated by the plant were combusted in the thermal oidizer. The source sampling served to measure the concentration of various pollutants emitted from this point source. Attempts were then made to compare this information with ambient pollutant concentrations as determined by the air monitoring network. The source sampling program also served to demonstrate compliance to source emission standards. The parameters measured were as follows:

Elemental Analysis	Carbonyls
Arsenic Beryllium Cadmium	Nickel carbonyl Iron carbonyl
Fluorine Iron	Other Effluent Contaminants
Lead	SO ₂
Nickel	NO _x
Selenium	$H_2\hat{S}$
Titanium	Organics
	Particulates

Sampling and analytical procedures are noted in Appendix B.

Fugitive Emissions

The Fugitive Emissions Program was planned at the SYNTHANE pilot plant. An inventory had been performed in March, 1978 but no sampling had been undertaken due to the pilot plant operating schedule. Sources that were considered included: baghouse, char pond surface, oil water sump, decanter safety flare, high pressure valves, coal grinding vent system, slurry/filter feed tank, CO₂ vent, wastewater receiver tank vent and open top holding tanks. The actual sampling was expected to begin during the early months of 1979.

II. Water Monitoring

The water monitoring program conducted at the SYNTHANE pilot plant consists of three phases--Surface Water Control, NPDES Sampling and Continuous Water Monitoring.

Surface Water Control

The surface water control program was designed to minimize contamination of site effluent from spills and non-point source discharges. It has become an integral part of the Spill Control and Countermeasure Plan (SPCC), as well as the water pollution control program. Pilot plant operations are characterized by frequent maintenance procedures. This results in unusually high potential for spills to occur and debris to accumulate in process areas. These characterics added to the inherent coal handling problems present a potentially significant surface water contamination problem. In an attempt to mitigate

pollutant loading in the plant effluent, paving and trenching of the process area was undertaken. The concrete paving was sloped to a trench and covered with an iron grill. The trenching carries the surface runoff to two holding tanks (15,000 gal each). The original plan was to collect the surface runoff in the tanks and upon accumulation to analyze the water. If the analysis fell within a specified range the water could be discharged as a batch process. The original plan also provided that during extended periods of rain the initial runoff could be collected in the holding tanks. After the runoff has been washed clean, a valve would redirect the water runoff directly to the storm sewer. As experienced at the pilot plant the effective execution of a surface water control program requires good housekeeping, strict control procedures and close surveillance to minimize the amount of contaminated runoff.

NPDES Sampling

The <u>Code of Federal Regulations</u>, <u>Title 40</u>, requires that owners or operators of a facility discharging via a point source must possess a National Pollutant Discharge and Elimination System (NPDES) permit. This NPDES permit includes effluent limitations to which the owner or operator must demonstrate compliance through a routine sampling and analysis program.

The SYNTHANE pilot plant was issued a NPDES permit, effective July 28, 1977, by the U.S. EPA. Recently the NPDES program has been reorganized whereby the administrative responsibilities are being assumed by the Commonwealth of Pennsylvania, Department of Environmental Resources. This change in administrative responsibility from federal to state levels has already evolved in most other states. The reorganization is expected to change some permit parameters. The permit currently contains discharge limitations for five effluent points. These include a sewage treatment plant, cooling tower blowdown, demineralizer, boiler blowdown (high and low pressure). These five discharge points have been determined to include all discharge contributions to the receiving stream. The justification for this decision was delineated in a December 4, 1975 memorandum to U.S. EPA. The EPA regional office agreed that the PETC proposed sampling sites were more feasible and representative than the single sampling point originally proposed by EPA.

Continuous Water Monitoring

The initial siting of the SYNTHANE pilot plant included the excavation of the valley in which the plant is situated which resulted in the diversion of the natural drainage through a 48" interceptor line, Figure 2. The pilot plant was then constructed over this interceptor along with a 15" storm drain and a 12" perforated drain. The five pilot plant discharge points (previously outlined in NPDES Section) contribute to these three underground drains and are subsequently mixed to form a single effluent stream in a 10' x 10' x 10' concrete box that is located (underground) at the eastern boundary of the pilot plant.

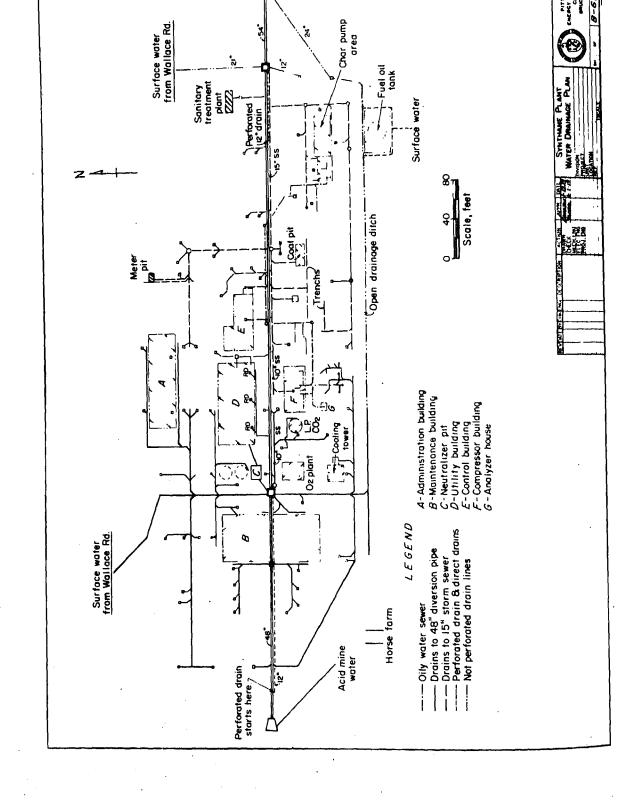
The approach taken to characterize the pilot plant contributions to the receiving stream includes five continuous water monitors, one at the plant inflow at the 48" line, one at the discharge end, one each at the 12" and 15" lines and one to measure the combined flow of the 10' x 10' x 10' concrete box. Flow measurements have been attempted at both inflow and outflow. At this time the "other sources" (storm drainage and road runoff problems) that have contributed to the total plant runoff are being separated out by a rerouting of surface water drainage lines. This source contribution has complicated sampling by blocking lines and interfering with flow measurements. Upon completion of this rerouting of storm drainage and road runoff the original continuous sampling schedule was to be resumed.

At the present time the continuous monitoring network consists of one 24-hour continuous sampler and flow meter at the plant inflow and three continuous samplers plus a flowmeter at the outfall. The samples are visually inspected and general pollutant analyses are performed if determined necessary. The analysis could be performed by the on site Lummus Lab or through a local university contract.

Parameters measured in the water monitoring program for most sampling points include: biological oxygen demand (BOD-5), fecal coliform, conductivity, oil and grease, phenol, pH, NH₃, suspended solids, total dissolved solids (TDS), chemical oxygen demand (COD) and iron.

III. Noise

The noise monitoring program at the SYNTHANE pilot plant consisted of two phases: an ambient noise assessment and an inplant noise assessment.



Ambient Noise Assessment

A background noise assessment was conducted for the SYNTHANE pilot plant during September-October 1977. The concern in this program phase was strictly in regard to the noise emission from the plant rather than with respect to any of its operating characteristics. The principal noise producers in the plant were divided into the following categories:

Mechanical: grinders, pulverizers, gears, conveyors.

Flow Devices: fans, blowers, compressors, valves.

Combustion: furnaces, flares, heaters.

Electromechanical: generators, motors, transformers, circuit breakers.

Augmenting the operating noises were noises produced by maintenance operations and those resulting from truck movement.

A two-step approach was utilized in acquiring the needed data. The first step was field recording of the noise and the second was laboratory analysis of the recorded data.

The field recording system consisted of a sound level meter, a battery powered tape recorder, and an acoustic signal generator for providing the necessary reference signal. A windscreen was used over the input microphone to eliminate wind generated noise. Recordings were not made whenever the wind speed exceeded 15 miles per hour. The frequency response of the sound level meter was set in the A-weighting mode, as this practice will tend to reduce chances of either overloading the sound level meter or saturating the magnetic tape. The sound level meter also served as a calibrated attenuator for the tape recorder. On playback, the signal from the tape recording was fed through a calibrated attenuator into a level recorder. The signal coming out of the level recorder was then sorted by a distribution analyzer into various level intervals. A 5 dB interval was chosen for this study.

The tape recorder had a dynamic range of about 45 decibels. By appropriately adjusting the input level at the start of a recording session, overloading was never observed. The period of measurement spanned the better parts of September and October. The data were tabulated to enable any future correlation of the noise data with the plant operation log and other pertinent environmental data.

The data revealed that noise emission from the plant has a significant impact upon an area as far as about a mile to the east of the plant. It was also determined that a flare stack located atop the thermal oxidizer was a significant contributor of noise emissions. The flare subsequently was modified to reduce the venturi effect and the noise level was reduced to an acceptable level. This noise monitoring program has made it apparent that much lower noise levels are required in rural areas where ambient levels are generally low. The variability of noise level tolerances due to background levels should be an important consideration in siting plant operations.

In-Plant Noise Assessment

The in-plant phase of the noise monitoring program was planned and awaited resumption of the pilot plant operations. The initial monitoring and data collection was expected to begin in Fiscal Year 79. Equipment which was to be used in this study included: precision sound level meter with octave band analyzer; tape recorder, real time noise analyzer; and strip chart recorder. The in-plant noise assessment was to concentrate on the areas categorized in the ambient noise assessment section of this paper.

Occupational Health Program

Many of the occupational health programs for coal conversion processes have been based on the literature documenting hazards of coke oven emissions. Coke oven emissions and coal conversion emissions are considered by some experts to be similar in various categories. It is generally viewed by these health scientists that it would be prudent to develop model occupational health programs similar to those used in coke oven hygiene programs until a knowledge of the specific hazards can be discerned. The investigations to determine the specific worker health hazards of the SYNTHANE process have been underway. Included in these investigations were industrial hygiene type monitoring and biological laboratory testings. Until specific hazards and problem areas were known, protective clothing was worn by workmen who were exposed to potentially hazardous waste products and emissions.

operations were also considered for use or proposed in the SYNTHANE program.

The SYNTHANE pilot plant program was assessed in preparation of "Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants", prepared by Enviro-Control for NIOSH.

Solid Waste Program

The recent passage of the Toxic Substance Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA) has made it increasingly evident that more attention must be made to acceptable disposal and handling of solid wastes. The solid wastes program at the SYNTHANE pilot plant has accelerated in recent months. This acceleration included a project conducted by the EC Division, evaluates solid waste products for toxicity, leachability, mutagenicity and carcinogenicity. This is being conducted through carefully controlled laboratory studies. Leachate studies have been completed on specific waste products in the past. These studies indicated that char pond solids have the potential to create a leachate problem and require special handling. Studies have been conducted on the dewatered char from the SYNTHANE process. This char has been determined to cause no leachate problem and may be disposed of in conventional landfill operations. Data from biological testing concerning the mutagenicity of coal tar products from the SYNTHANE pilot plant process are expected shortly. These data will define parameters for more advanced toxicity testing to provide for environmentally sound disposal practices.

SUMMARY

The U.S. Department of Energy (DOE), as part of our country's overall efforts to address and resolve energy issues, has engaged in a broad range of R&D activities. A major emphasis of these efforts has been focused on the utilization of coal as an energy source. Coal conversion technology is currently developing in several specific areas. The objective of this paper has been to discuss the environmental activities related to one specific coal conversion process referred to as the SYNTHANE Coal Gasification Process.

demonstration units. Consideration of problem areas identified at SYNTHANE will be useful as a preventive tool to be utilized in the design and implementation of these similar programs

Some highlighted considerations in conducting environmental assurance programs as identified through the SYNTHANE environmental efforts appear in Appendix C.

DOE has assumed the major responsibility for environmental health aspects of its technologies. This includes the evaluation and assessment of the environmental impact of each developing technology, such as SYNTHANE. The overall practicability and commercialization of these energy technologies depend heavily on their ability to comply with existing and future environmental/health regulations. It seems prudent to assess and develop simultaneously the environmental control technologies and process technology. The early incorporation of environmental concerns will serve to minimize the ultimate environmental impact and perhaps reduce or eliminate the expense of retrofitting control devices on the final process.

Sampling methods utilized in the mobile van data collection activity:

- 1. SO₂ one hour impinger samples at 840 cc/min. using West-Gaake Absorbing Reagent. Analysis was by colorimetry using pararose-aniline-formalhyde-Method B.
 - REF. Method 42401-01-69T Intersociety Committee Methods of Air Sampling and Analysis.
- 2. H₂S one hour impinger samples at 1.30 1/min. using cadmium hydroxide slurry as absorbing reagent. Analysis was by colorimetry of methylene blue produced by the reaction of sulfide with reagents.
 - REF. Method 42402-01-70T Intersociety Committee Methods of Air Sampling and Analysis.
- 3. Phenol one hour impinger samples at 1.85 1/min. using 5% sodium carbonate as absorbing reagent. Analysis was by colorimetry using 4-aminoantipyrine reagent.
 - REF. Standard Methods for Water and Waste Water Analysis, 13th. Edition.
- 4. Coefficient of Haze Particulate was sampled using the AISI Paper tape sampler.
 - REF. ASTM D-1704-61 Standard Method of Test for Particulate Matter in the Atmosphere.

Sources," except as follows:

- 1. Due to the high temperatures present in the thermal oxidizer stack, a water-cooled sampling probe was used. The portion of the probe not exposed to the high temperatures was heated to prevent condensation.
- 2. Due to difficulties encountered rigging the traditional probe/impinger box configuration, a heated teflon house was included to allow a flexible connection between the sampling probe and impinger box. The hose temperature was maintained at 250°F or greater to prevent condensation. Acetone washing from the hose was included with that of the probe.
- 3. Sampling for fluoride emissions (Method 13A) was combined with the particulate sample. A stainless steel screen filter support was used rather than a fitted glass type. The glass support has been shown to retain fluoride (Amendments to Reference Methods 13A and 13B, Federal Register, Vol. 41, No. 230, Nov. 29, 1976, Title 40, Part 60). Test methods and procedures for 13A and 13B appear in the Federal Register, Vol. 40, No. 152, Aug. 6, 1975.
- 4. The third impinger contained caustic, rather than being dry, to collect arsenic and to protect equipment from acid gases.

Metals

Arsenic, beryllium, cadmium, lead, and nickel contents of the particulate catch were determined by atomic absorption. Impingers 1, 2 were also ether-chloroform extracted to determine condensible organics.

NO^{x}

U.S. EPA Method 7 was utilized. The sampling train equaled that of Figure 7-1 of the Method.

SO_2 , H_2S

SO₂ by U.S. EPA Method 6 and H₂S measurements were combined, according to the State of Texas procedure. The sampling train equaled that of the procedure except the glass fiber filter had to be omitted due to the high temperature. However, the catch was filtered using a glass fiber filter prior to analysis. A quartz sampling probe was substituted for the pyrex due to high temperatures.

Since the State of Pennsylvania requires a different SO₂ analysis, the sampling and analytical procedures followed the APCD, County of Los Angeles, Method for Oxides of Sulfur, page 85, Source Testing Manual, 1965. The instack thimble had to be omitted due to the high temperature, but the catch was filtered using a glass fiber filter prior to analysis.

as reconstruct annough the plantage environmental ellores;

Proper segregation of contaminated wastewater from other aqueous effluents. This will facilitate optimum sampling accessibility and representativeness and minimize the volume of wastewater requiring treatment.

Precise documentation of operations schedules concerning air emissions. This documentation is necessary to correlate field ambient air monitoring with operations emissions to yield meaningful evaluations of various pollutant impacts from specific point sources.

Appropriate considerations of community noise levels in conducting the site selection process. Siting in the vicinity of a residence with conservative background noise levels has a much greater adverse impact than an area with higher community noise levels.

The types of solid waste generated by the plant should be considered in the siting process. Certain types of waste require special disposal techniques and facilities. The proximity of the appropriate disposal facilities is important due to high transportation costs and stringent DOT and EPA regulations.



FOSSIL FUEL POWER GENERATION - ADVANCED METHODS (II)

Chairman: Stephen Freedman

Co-Chairman: Jerry Pell

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J. S. Halow, U. Grimm, J. S. Mei

U.S. Department of Energy Morgantown Energy Technology Center

A program was initiated late last year at the Morgantown Energy Technology Center, Department of Energy to demonstrate a 90 percent sulfur retention capability in the 18-inch atmospheric fluidized-bed combustion (AFBC). This program was undertaken in response to concerns about the impact of possible New Source Performance Standards (NSPS) proposed by the Environmental Protection Agency in sulfur emissions. A high volatile bituminous coal with 4.42 percent of sulfur content was selected for this study. Greer limestone as well as tymochtee dolomite were used as bed material and sorbent. Combustion tests were carried out at various operating conditions to develop AFBC engineering and emissions data on this high sulfur coal. Ninety or greater percent of sulfur retention was attainable in several of the eighteen balance periods depending on operating conditions. The results of the present tests clearly demonstrate that the proposed new standards for sulfur dioxide emissions can be met by AFBC's. The required operating conditions could, however, have serious impact on AFBC economics.

GAS TURBINE CATALYTIC COMBUSTORS FOR COAL DERIVED FUELS

Warren W. Bunker
U. S. Department of Energy
Energy Technology

Catalytic combustion for gas turbines is a unique process which promises very low NO emission levels at high efficiencies and comparable pressure drops. The Department of Energy (DOE) is expanding the catalytic work of EPA and NASA into the area of coal-derived fuels, both gases and liquids. On-going programs for the combustion of low Btu gas, medium Btu gas, and heavy liquids are described. Future plans for possible field tests are discussed.

U.S. Department of Energy

Grand Forks Energy Technology Center

The atmospheric fluidized-bed combustion of Western and Gulf Coast lignites and subbituminous coals offers a method of utilizing these low-sulfur, high-alkali coals with possibly little or no added sulfur sorbent. Tests using a 60inch atmospheric fluidized-bed combustor showed that eight of ten Western coals could be burned without addition of limestone and meet the standard of 1.2 lb SO₂/MM Btu. The downward revision in the NSPS will change the design criteria for these low-rank coals, as well as high-sulfur bituminous coals, but the sulfur retention on ash will still make a substantial contribution.

For the low-rank coals tested, the calcium-to-sulfur ratio ranged from 1 to over 4, and the sulfur retention from nearly 0 to over 90 pct. Reinjection of primary cyclone fly ash increased sulfur capture significiantly, but not sufficiently to insure compliance of all low-rank coals under the NSPS standards. Bed temperature influenced sulfur retention in the range of 1250° to 1600°F, with maximum retention at 1400°F without ash reinjection and 1500°F with ash reinjection. During operation some of the coal ash agglomerated within the bed and was also deposited on the tube walls.

Tests for characterizing gaseous and particulate emissions from the AFBC have been performed; preliminary results of these tests are presented in this paper. The physical and chemical characteristics of the fly ash produced in the AFBC with and without cyclone ash recycle are examined.

CONTROL OF NITROGEN OXIDE EMISSIONS IN COAL-FIRED, OPEN-CYCLE MHD POWER PLANTS

Joseph Epstein

U. S. Department of Energy

Energy Technology

The control of nitrogen oxide (NOx) emissions from coal-fired power-plants, including Magnetohydrodynamic (MHD) systems is an issue which most often appears in the evaluation of a new technology. Since the 1960's, the MHD community has given considerable attention

Present information indicates that both current and future NOx standards can be met by the MHD process even though no credit is provided for the significant increase in net plant efficiency over conventional power-plant systems.

Presently available results from experiments as high as 8 MWt and from calculations based on experimentally derived kinetics data have served to empirically identify realistic NOx control techniques. The preferred system operation is to: (a) operate the coal combustor fuel rich, (b) cool the gas slowly in a radiant boiler downstream of the MHD channel/diffuser, (the radiant boiler is the key component in MHD NOx control), and (c) add additional air to the radiant-boiler exhaust, at a temperature high enough to complete combustion but low enough to minimize the tendency to form additional NOx. These concepts are discussed in detail along with experimental and analytical results that have been obtained to verify that the method of control is technically sound and practical. Current DOE-sponsored R&D efforts are aimed at optimizing the method and at formal demonstration in suitable facilities.

CONTROL OF SULFUR DIOXIDE AND PARTICULATE EMISSION IN MHD POWER SYSTEMS USING HIGH SULFUR COAL

K. E. Tempelmeyer, Terry Johnson, Paul Blackburn Argonne National Laboratory

Joram Hopenfeld
U.S. Department of Energy
Energy Technology

W. Spurgeon

Gilbert Associates

MHD power generation systems offer an attractive opportunity to utilize high sulfur coal and yet reduce the emissions of sulfur oxides as well as the oxides of nitrogen and particulate matter. Interaction of sulfur compounds with the potassium seed material added to the coal or combustion products to make the MHD process work results in an attendant reduction of SO₂ emissions of 80 to 90 percent. The sulfur compounds released in the combustion of coal interact with potassium forming solid potassium sulfate. The potassium must be recovered in an MHD system and reprocessed in order to

results are compared with available experimental information, which summarizes the effectiveness in which SO₂ emissions are compared to present EPA standards, as well as anticipated emission standards for SO₂ in the future. Finally, some comments are made as to the applicability of this control measure as a retrofit means to control SO₂ emissions in existing utility boilers.

FLUE GAS CLEANING FOR PRESSURIZED FLUIDIZED-BED COMBUSTORS

Irvins Johnson et al.
Argonne National Laboratory

Studies underway at ANL to clean up the hot flue gas from a PFBC so that it will be suitable for gas turbine use will be reviewed. Granular limestone beds and high efficiency cyclones are under study for particulate removal. Acoustical preconditioning of the flue gas is being evaluated as a method to increase the particulate size in order to increase the efficiency of cyclones. Two laser on-line particle size and concentration analyzers have been experimentally evaluated. The use of hot granular bed filters for the removal of gaseous alkali metal compounds is under study. Two sorbents, diatomaceous earth and activated bauxite, have been found to be highly effective for the removal of gaseous NaCl and KCl from hot flue gas.

REDUCING THE ENVIRONMENTAL IMPACT OF SOLID WASTES FROM A FLUIDIZED-BED COMBUSTOR

Irving Johnson, R. B. Snyder, W. M. Swift and A. A. Jonke Argonne National Laboratory

The effectiveness of three options for the reduction of the environmental impact of solid sorbents used to control the SO₂ emission from fluidized-bed coal combustion systems will be compared. These options are: (1) pretreatment of the sorbent (use of chemical additives such as NaCl or CaCl₂) to increase its reactivity with SO₂, (2) regeneration and reuse of the sorbent, and (3) the use of synthetic sorbents. The quantity of waste generated decreases in the order (1) to (3); the cost increases in the order (1) to (3). The use of chemical additives and the regeneration and reuse of the limestone are viable options. The high cost of synthetic sorbents currently available rule out this option from further consideration.

J. S. Halow, U. Grimm, J. S. Mei

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ABSTRACT

A program was initiated late last year at the Morgantown Energy Technology Center, Department of Energy to demonstrate a 90 percent sulfur retention capability of an atmospheric fluidized-bed combustor (AFBC) burning a high sulfur coal. This program was undertaken in response to concerns about the impact of possible New Source Performance Standards (NSPS) proposed by the Environmental Protection Agency on the application of AFBC technology. A high volatile bituminous coal with 4.42 percent sulfur content was selected for this study. Greer limestone as well as Tymochtee dolomite were used as sulfur sorbents. Combustion tests were carried out at various operating conditions to develop AFBC engineering and emissions data on this high sulfur coal. Ninety or greater percent of sulfur retention was attained in nine of the nineteen balance periods. Eighty-five or greater percent sulfur retention was attained in fourteen of the nineteen balance periods. The results of the present tests clearly demonstrate that the proposed new standards for sulfur dioxide emissions can be met by AFBC's.

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Fluidized-bed combustion of coal is a process that has been under study since the early 1960's in both England and the United States. This process offers a means of burning a variety of coals and other fuels in an environmentally acceptable manner.

In a fluidized-bed combustor, coal is burned in a bed of inert ash and lime-stone or dolomite fluidized by the injection of air through the bottom of the bed at controlled rates. The limestone or dolomite in the bed reacts with the sulfur dioxide released by the combustion of the coal, and forms a solid sulfate. Heat is extracted by tubes immersed in the bed and above the bed. Advantages of the AFBC include: Early commercial availability, a projected competitive cost, controllable emissions of SO and NO, fuel flexibility, and a solid spent sorbent stream that can readily be disposed of along with the coal ash.

At present, New Source Performance Standards (NSPS) limits sulfur dioxide (SO_2), nitrogen oxides (NO_2), and particulate matter that can be emitted from a utility boiler stack. Suppression of SO_2 and NO_2 in a fluidized-bed boiler is achieved in the combustion process. The combustion stability provided by the fluidized bed and the balance of heat input and removal from the bed maintains combustion at temperatures below the ash fusion point, and low enough to permit the conversion of limestone and SO_2 to sulfate and to inhibit the formation of nitrogen oxides. To meet NSPS for particulates, conventional mechanical collector and dust removal precipitators or filters will likely be adequate.

This paper discusses SO_2 capture in an AFBC when burning high sulfur coals. Experimental tests burning a high sulfur bituminous coal were conducted in the Morgantown Energy Tecnology Center's 18-inch diameter combustor. This study was undertaken in response to concerns about the impacts of proposed New Source Performance Standards on AFBC technology.

Variables Effecting Sulfur Capture

Sulfur capture is dependent on a number of design and operating variables as well as the sorbent used. A primary variable which can be readily controlled is the calcium to sulfur mole ratio. Increasing the Ca/S mole ratio increases the amount of active sorbent in the bed, thereby increasing sulfur capture. Also of importance is the bed temperature since the $\rm SO_2/sorbent$ reaction is temperature dependent. An optimum sulfur capture temperature of around 1550°F is common for many sorbents. In designing and operating AFBC's, it is desirable to minimize Ca/S mole ratio since high sorbent usage significantly impacts AFBC economics through the cost of sorbent, parasitic heat losses through calcination, and increased spent sorbent disposal costs.

also increases gas residence time and, therefore, increases sulfur capture. These variables along with the Ca/S mole ratio need to be balanced to achieve efficient sulfur capture with an economically viable design. Sorbent variety also has a significant effect on sulfur capture.

Reported pilot plant data (1,2,3) has shown sulfur retention results of 90 percent or greater on a variety of fuels and sorbents. Test results reported in this paper provide additional data. Also, since the tests were performed to specifically meet high sulfur capture conditions, the current data allow correlation with operating variables.

Characteristics of Fuel and Sorbents Used in Tests

The coal used in this investigation was a bituminous-A, high volatile coal with a sulfur content of 4.42 percent. It's origin was the Pittswick Coal Company in National, WV, approximately 5 miles south of Morgantown, WV. The company is mining a coal formation better known as the Sweckley seam. The chemical analysis of this coal is given in Table 1.

Table 1 Composition of Pittswick Coal

Moisture %	0.94	Ash analysis	<u>5_%</u>
Ash %	14.04	SiO_2 4	4.90
Sulfur % Total	4.42	$A1_20_3$ 23	2.91
Pyritic	2.36	Fe_2O_3 2:	2.71
Hydrogen %	5.18	CaO	1.06
Total Carbon %	69.45	MgO	0.82
Nitrogen %	1.15	Na ₂ O	0.28
Oxygen %	4.85	K ₂ O	2.08
		P_2O_5	0.07
Btu/lb	12,700	$\overline{\text{TiO}}_{2}$	1.18
		SO_3	1.00

Table 2 Screen Analysis of Coal

Size Range	$1/4 \times 0, \%$	$1/8 \times 0, \%$
1/4"-4 mesh	8.1	0.2
4-8 mesh	37.9	8.8
8-16 mesh	21.9	20.7
16-30 mesh	13.5	25.5
30-50 mesh	6.9	17.8
50-100 mesh	3.9	12.1
100-200 mesh	3.0	8.2
200-	4.8	6.8

The sorbents used in the test program were Greer limestone and Tymochtee dolomite. Greer limestone is the predominant limestone in the area of West Virginia's high sulfur coals and its sorbtion characteristics can be classified as good to very good. Tymochtee dolomite was chosen because thermogravimetric analyzer (TGA) studies by the Argonne National Laboratory have classified this material as one of the best sorbents. It originated in Huntsville, Ohio, a dolomite formation approximately 50 miles northwest of Columbus, Ohio. The chemical analysis of both materials are listed in Table 3. The sorbents were air dried, crushed, and screened before being fed to the FBC at the top of the expanded bed. The size distributions of sorbents used in the tests are presented in Table 4.

Table 3 Composition of Sorbents

Elemental Analysis	Tymochtee Dolomite	Greer Limestone
As Carbonates* CaCO ₃ % MgCO ₃ %	53.88 41.49	86.2 5.34
As Oxides* CaO% MgO% CO2%	28.04 19.84 42.05	44.8 2.15 47.37

^{*} Balance is moisture, Al_2O_3 , SiO_2 , and traces.

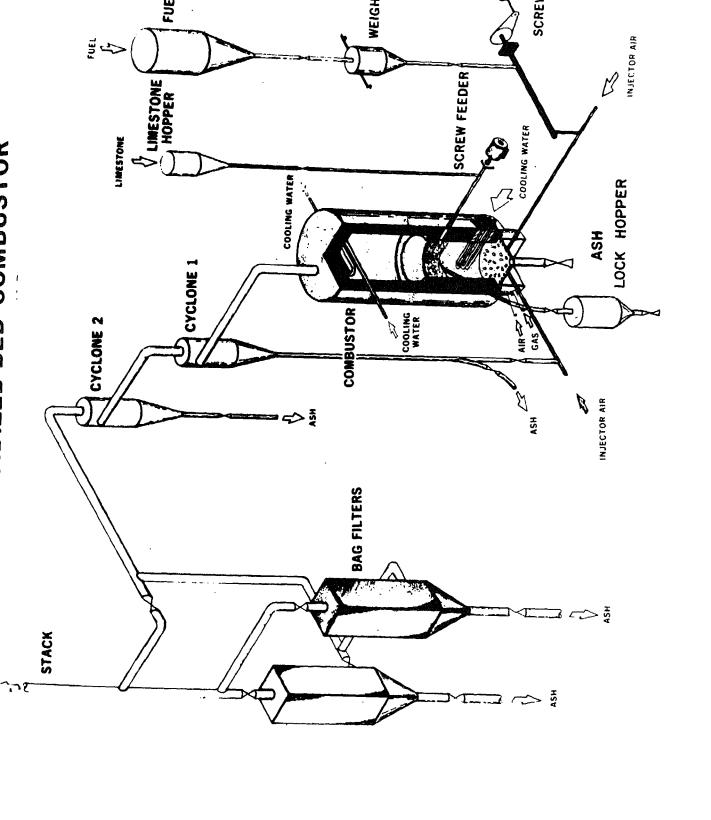
Size Range	Greer Lime	stone Wt %	Tymochtee Do	lomite Wt%
	1/4 x 10 mesh	1/4 x 30 mesh	1/4 x 28 mesh	5/10 x 3/3
1/4"-4 mesh	39.8	2.28	0.2	47.87
4-6 mesh	49.9	34.8	27.7	40.40
4-8 mesh 6-10 mesh	9.7	74.0		49.40
8-16 mesh	<i>y</i> .,,	30.34	20.4	1.53
10-12 mesh	0.4	₩. ==	une 🏎	
16-30 mesh		14.61	17.8	.08
30-50 mesh		5.32	10.1	.16
50-100 mesh		4.03	6.4	.08
-100		8.59	17.4	.88

EXPERIMENTAL FACILITY AND START UP PROCEDURE

The experimental facility at the Morgantown Energy Technology Center for fluidized-bed combustion of low-quality fuel feasibility studies is shown schematically in Figure 1. It is basically a refractory-lined cyclindrical combustor having an internal diameter of 0.46 m (18 inches) in the 1.14 m (45 inches) high bed region with an attached 0.69 m (27 inches) high expanded freeboard section of 0.61 m (24 inches) diameter.

The combustor contains a set of hair-pin-type water cooled heat exchanger tubes located in the bed region and a single pass water cooled heat exchanger in the expanded freeboard. Coal is metered from a hopper and is fed into a fuel injection chamber by a screw feeder. The coal is then injected into the bed near the base of the conical air distributor plate by compressed air. Limestone, when used, is metered from a hopper and fed by a screw feeder directly into the top of the expanded bed. Entrained particulates in the flue gas leaving the combustor are removed by two stages of cyclones followed by bag filters. Particulate matter removed by the primary cyclone is reinjected into the bed for additional carbon burnup. Flue gas leaving the combustor is continuously sampled and analyzed. CO and CO₂ are determined by non-dispersive infra-red analyzers. A chemiluminescence analyzer is used to determine NO and NO₂. SO₂ and total hydrocarbon analyses are made by a flame photometric analyzer and a flame ionization analyzer, respectively, and O₂ by a paramagnetic analyzer.

Start up of the unit is accomplished by preheating the lower part of the combustor to 816°C (1500°F) with premixed natural gas and air. When the desired temperature level is reached, approximately 23 kg (50 lb) of bed



continued with minimum sorbent addition until sulfur dioxide is seen in the flue gas. Then desired operating conditions are established and the unit allowed to stabilize before a data-taking balance period is started. Typical balance periods are 10 hours in duration.

RESULTS OF SULFUR RETENTION STUDIES

It has been mentioned previously that the present study was undertaken in response to the concern about the impact of the proposed NSPS of 90 percent sulfur retention on AFBC technology. The studies, therefore, were carried out at conditions which could lead to high sulfur retention in the bed. The variables investigated for the present study have been Ca/S mole ratio, fluidized-bed temperature, gas residence time, type and particle size of sorbent. Table 5 presents a summary of the experimental conditions and the sulfur retention results for the experiments carried out in this study. The analysis of the results are discussed below.

Figure 2 illustrates the effect of average bed temperature on the percentage of sulfur captured by two different types of sorbent, Greer limestone and Tymochtee dolomite. Data for Greer Limestone show a clear temperature dependence (solid curve) in spite of variations Ca/S ratio, gas residence time and sorbent particle size. A maximum reactivity around 1550°F is evident. Tymochtee Dolomite does not show a clear trend in this data. An optimum temperature range for sulfur capture is observed for Greer limestone between 1500° to 1600°F. As seen, 90 percent or better sulfur retention can be obtained over the optimum temperature range.

The effect of Ca/S mole ratio on sulfur retention is shown in Figure 3 for the two sorbents at a bed temperature range between 1500° to 1600° F where sulfur capture had been optimized. The present results indicate that for this particular high sulfur coal and Greer limestone, a calcium-to-sulfur mole ratio of 2.0 would be adequate to assure compliance with the proposed NSPS of 90 percent sulfur removal. With Tymochtee Dolomite, a Ca/S ratio of 1.5 appears to be adequate to meet a 90% sulfur retention with the revised NSPS of 85 percent sulfur retention, lower Ca/S ratios would appear to be sufficient in the optimum bed temperature range and with the 0.75 sec to 1.00 sec residence times used in these tests, but the data is insufficient to draw a firm conclusion at this retention level. The calcium-to-sulfur ratio required to maintain 90 percent sulfur removal, however, is lower than the projected value (Ca/S \cong 2.8) by Westinghouse kinetic model (4) and by the MIT model (Ca/S \cong 3.1) (5) at similar operating conditions.

TABLE 5. SUMMARY OF EXPERIMENTAL CONDITIONS AND SULFUR RETENTION RESULTS

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		Particle	Particle	Bed	Superfic.	Bed	Resid.	co/s	$S0_2$	50_2	Su
Run	Sorbent	Size	Size	Temp.	Velocity	Depth	Time		Emission	Emission	Det
No.	Type	(Sorbent)	(Coal)	(°F)	(ft/sec)	$(\hat{\mathbf{f}}\mathbf{t})$	(sec)	2	(mdd)	(1b/10 ⁶ Btu)	
1/1	G. Lime.	1/4"x10 mesh	1/4×0"	1524	2.99	3.00	1.00	3.91	240	0.54	9
1/2	G. Lime.	1/4"x30 mesh	1/4×0"	1470	2.91	3.00	1.03	2.62	949	1.42	8
1/3	G. Lime.	1/4"x30 mesh	1/4×0"	1533	3.03	3.00	0.99	3.44	255	0.62	9
1/4	G. Lime.	1/4"x30 mesh	14/x0"	1536	3.45	3.00	0.87	2.05	259	0.63	6
1/5	G. Lime	1/4"x10 mesh	1/4×0"	1582	3.51	3.00	0.85	1.82	344	0.56	6
1/6	T. Dolom.	1/4"x28		1465	3.43	3.00	0.87	1.21	006	1.67	7
1/7	T. Dolom.	1/4"x28	ĺ	1444	3.39	3.00	0.88	1.24	300	0.59	6
1/8		1/4"x28	1	1546	3.51	3.00	0.85	08.0	855	1.44	8
1/9	T. Dolom.	5/16"x3		1547	3.51	3.00	0.85	1.20	412	0.75	8
1/10		5/16"x	1/8×0"	1556	3.82	3.00	0.79	1.43	439	96.0	8
1/11	1	5/16"x3	1/8×0"	1554	3.95	3.00	97.0	1.44	303	0.57	ان
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2/1	G. Lime.	1/4"x10 mesh	1/4×0"	1653	3.51	3.00	0.85	2.67	414	0.76	Ø
2/2	G. Lime.	1/4"x10 mesh	1/4×0"	1507	3.27	3.00	0.92	1.87	112	0.19	9
2/3	G. Lime.	1/4"x10 mesh	1/4×0"	1463	3.13	3.00	96.0	2.13	1427	2.78	9
2/4	G. Lime.	1/4"x10 mesh	ľ	1670	3.50	3.00	98.0	2.82	667	0.88	8
2/4R	1	1/4'x10 mesh		1637	3.58	3.00	0.84	2.68	650	1.10	æ
2/5		1/4"x10 mesh		1555	3.44	3.00	0.87	2.99	155	0.31	9.
2/6	G. Lime.	1/4"x10 mesh		1482	3.30	3.00	0.91	4.21	471	1.03	89
2/7	G. Lime.	1/4"x10 mesh		1562	3.42	3.00	0.88	3.91	152	0.39	6
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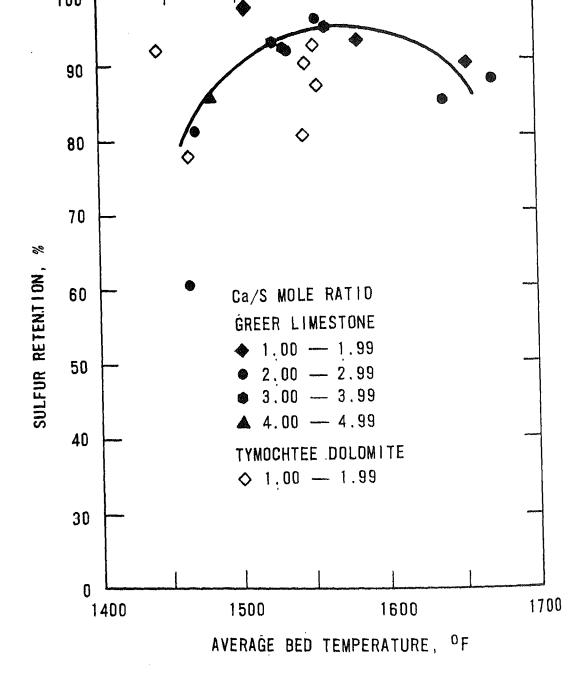


FIGURE 2. Effect of Average Bed Temperature on Sulfur Retention

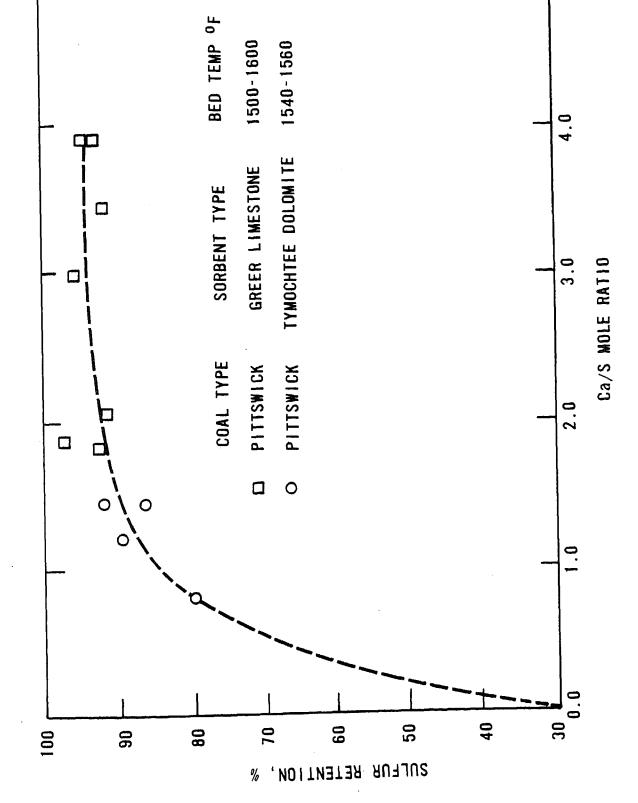


FIGURE 3. Effect of Ca/S Mole Ratio on Sulfur Retention